UNIVERSITY OF MAINE
LIBRARY

Class no. 537.86

Book no. C191+

Accession no. 65,952

Digitized by the Internet Archive
in 2026

https://archive.org/details/thermoelectromot0000henr

THERMO-ELECTROMOTIVE FORCE IN ELECTRIC CELLS

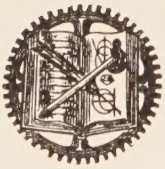
THE THERMO-ELECTROMOTIVE FORCE BETWEEN A METAL AND A SOLUTION OF ONE OF ITS SALTS

BY

HENRY S. CARHART, Sc.D., LL.D.

PROFESSOR EMERITUS OF PHYSICS, UNIVERSITY OF MICHIGAN; MEMBER, AMERICAN PHYSICAL SOCIETY; AMERICAN ELECTROCHEMICAL SOCIETY; AND INSTITUTION OF ELECTRICAL ENGINEERS (LONDON)

ILLUSTRATED



NEW YORK

D. VAN NOSTRAND COMPANY

EIGHT WARREN STREET

1920

COPYRIGHT, 1920, BY
D. VAN NOSTRAND COMPANY

FOREWORD

THIS book is composed mostly of the author's researches begun many years ago with those concerning the analysis of the temperature coefficient of voltaic cells. The earliest papers have suggested others, which have gradually been added. Some other matter germane to the subject has been taken from the work of others, notably that of Dr. Ernst Cohen on the Thermodynamics of Normal Cells.

The chapter on the electromotive force of concentration cells has special interest because it shows the application of the Helmholtz equation to such cells as distinguished from voltaic cells. It shows further that the Nernst equation is only the equivalent of the second term of the Helmholtz formula.

It will appear from this book that the thermo-emf between metals and solutions of their salts has manifold applications in electric cells. The wide application of thermo-emf it is hoped will appear as sufficient justification for the book itself.

H. S. C.

PASADENA, CAL.
Jan. 15, 1929

CONTENTS

PAGE

CHAPTER I

THERMO-ELECTROMOTIVE FORCE BETWEEN METALS..... 1

CHAPTER II

ELECTROMOTIVE FORCE BETWEEN METALS AND LIQUIDS.. 11

CHAPTER III

CONCENTRATION CELLS..... 20

CHAPTER IV

TEMPERATURE COEFFICIENTS..... 28

CHAPTER V

THERMODYNAMICS OF THE VOLTAIC CELL..... 43

CHAPTER VI

ELECTROMOTIVE FORCE OF CONCENTRATION CELLS..... 67

CHAPTER VII

THERMODYNAMICS OF CONCENTRATION CELLS..... 87

CHAPTER VIII

THERMODYNAMICS OF NORMAL CELLS..... 112

CHAPTER IX

THERMO-EMF WITHOUT TEMPERATURE DIFFERENCE.... 122

THERMO-ELECTROMOTIVE FORCE IN ELECTRIC CELLS

CHAPTER I

THERMO-ELECTROMOTIVE FORCE BETWEEN METALS

1. Reversible Heat. — "A reversible thermal effect occurring at any part of a circuit must be attributed to the existence at this point of a difference of potential existing independently of the current." In 1834 Peltier discovered that when an electric current is passed through a junction between different metals, there is either a development or an absorption of heat at the junction, according to the direction in which the current passes. Thus, let copper wires be soldered to the ends A and B (Fig. 1) of an iron wire. Then if the current passes in the direction AB, heat will be absorbed at A and this junction will be cooled; while at B heat will be generated and the junction will be heated. If the current is reversed, heat will be absorbed at B and generated at A. This reversible heat

effect shows that there is an emf between the copper and the iron at A, directed from copper to iron, and an equal one at B if the temperature of the junctions is the same.

When the current encounters an emf in the same direction as the current flow, energy is added to the current through the agency of the direct emf; and if the emf is thermoelectric, the energy is supplied by the heat of the junction,

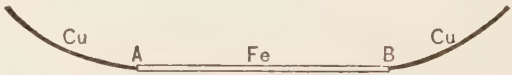


Fig. 1

which accordingly cools. The current from A toward B encounters at B a back emf which it works against. It therefore gives up energy to this junction which heats it, since the conditions do not permit the energy liberated there to take any other form. In an electric motor the energy spent in driving the current against the back emf of the armature takes the form of mechanical work; in electrolysis it becomes the energy of chemical separation. Peltier's discovery therefore proves the existence of an emf at a junction between different metals. The value of this emf at the absolute temperature T is $T\frac{dE}{dT}$.

The ratio of the increase of emf with respect to temperature, $\frac{dE}{dT}$, is known as the *thermoelectric power* of one metal with reference to another. If this were constant, the emf would be proportional to the absolute temperature. For a few pairs of metals it is nearly constant for a wide range of temperature. Hence the use of a metallic junction for measuring temperature.

The Peltier effect may be expressed in calories, in microvolts, or in joules. Expressed in joules the Peltier effect P_1 at the temperature T_1 is the mechanical equivalent of the heat liberated when one coulomb crosses the cold junction, and the effect P_2 is the mechanical equivalent of the heat absorbed at the hot junction at the temperature T_2 when one coulomb crosses this junction. Then, since the circuit is a reversible engine, so far as the Peltier effects are concerned we have by thermodynamics [1]

$$\frac{W}{T_2 - T_1} = \frac{P_1}{T_1} = \frac{P_2}{T_2},$$

where W equals the work done when one coulomb goes around the circuit. But this work is equal to the emf around the circuit. Hence

[1] Maxwell's Theory of Heat.

$$E = (T_2 - T_1)\frac{P_1}{T_1} = (T_2 - T_1)\frac{P_2}{T_2}.$$

If the Peltier effect were the only reversible one in the circuit and if the thermoelectric power were constant, the emf around the circuit, whose cold junction is kept at a constant temperature, should be proportional to the difference between the temperatures of the hot and the cold junction.

2. Thermoelectric Couples. — A thermoelectric couple, illustrated in Fig. 1, consists of two different metals joined together at their terminals; one junction may be joined through intermediate metals at one temperature. An emf is present at the two junctions, but so long as all the junctions are at the same temperature, the two emfs at the two junctions (such as those between iron and copper in Fig. 1) are equal, in opposite directions around the circuit, and counterbalance each other. There is no emf around the circuit unless one junction is at a higher temperature than the other. In that case the current will flow in a closed circuit in the direction of the larger emf at the warmer junction, and by means of the Peltier effect heat will be transferred from the hot junction to the cold one. Such a current, known as a thermoelectric current, was first observed by Seebeck in 1822,

The Peltier heat effect differs from the Joule effect in two respects: It is due to emf at the junctions and has no relation to resistance; it is proportional to the first power of the current strength, while the Joule effect, C^2Rt, is proportional to the square of the current.

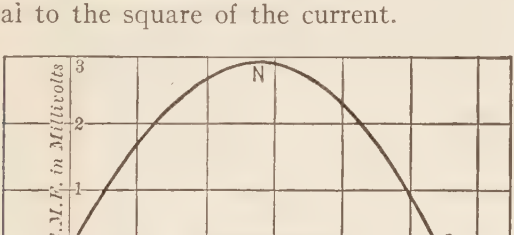


Fig. 2

3. The Neutral Point. — When the emf and the temperature difference of a thermal couple are plotted as coördinates, the resulting curve is approximately a parabola (Fig. 2). At the point where the tangent to the curve is parallel to the axis of temperatures the emf reaches its highest value and the thermoelectric power is zero. This point N is called the *neutral point* and the corresponding temperature the *neutral temperature*. At this point the Peltier emf becomes zero and the one metal is neutral to the other.

The curves for the different metals all pass

through the origin of coördinates, since the emf is always zero when both junctions are at the same temperature, 0° C., for example. The neutral temperature for a platinum-lead couple is −150° C., and for a zinc-lead couple, −260° C. For a copper-iron couple it is about 275° C. When the hotter junction passes the neutral temperature for any couple, the Peltier emf changes sign and the emf in the circuit falls. It becomes zero when the temperature of the hot junction is as far above the neutral temperature as that of the cold one is below it.

Since the curve connecting the circuit emf and the temperature difference between the junctions is a parabola, we may write

$$E = a(T_2 - T_1) + \frac{b}{2}(T_2 - T_1)^2$$

$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - 2T_1T_2 + T_1^2).$$

The constants a and b depend on the nature of the metals. Since T_1 is a constant, differentiating with respect to T_2 we have

$$\frac{dE}{dT_2} = a + 2\frac{b}{2}T_2 - 2\frac{b}{2}T_1 = a + b(T_2 - T_1) = \text{zero}$$

for the maximum value of E. Therefore

$$T_2 - T_1 = -\frac{a}{b} \text{ for the neutral point.}$$

If in the expression for $\frac{dE}{dT_2}$ above we substitute for $T_2 - T_1$ its value corresponding to maximum E, we have

$$\frac{dE}{dT_2} = a - b\left(\frac{a}{b}\right) = 0.$$

This expression shows that at the neutral point both the thermoelectric power and the Peltier effect are zero.

If $-\frac{2a}{b}$ is substituted for $T_2 - T_1$ in the expression above for E, we obtain $E = 0$. Thus if the temperature difference $T_2 - T_1$ for the maximum value of E is doubled, the emf of the circuit drops to zero.

4. Thermoelectric Diagram. — In the last article it was found that the thermoelectric power $dE/dT_2 = a + b(T_2 - T_1)$. This is the equation of a straight line. If therefore thermoelectric power and difference of temperature are plotted as coördinates, the result will be a straight line. In Fig. 3 thermoelectric powers between several metals and lead as the reference metal are plotted as ordinates per degree C. and temperatures of the hot junction as abscissae, the cold junction being kept at 0° C. Such a series

of straight lines compose a thermoelectric diagram. The point of intersection of any pair of lines is the neutral point for the two corresponding metals. Thus the copper-iron lines cross at 274.5°; this is therefore the temperature at which the thermoelectric power of these metals

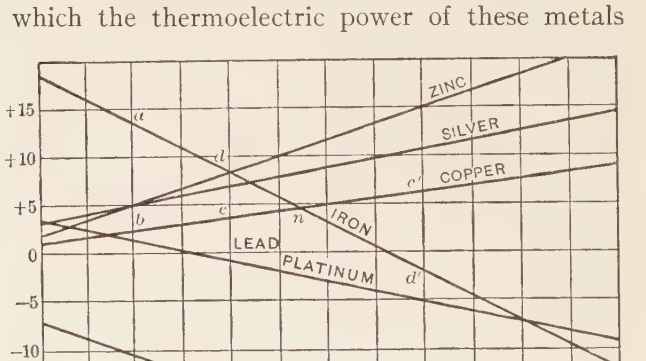


Fig. 3

becomes zero. It is also the neutral temperature for the pair. Figure 4 is the thermoelectric diagram for several metals compared with lead. The palladium-copper lines if produced would meet at −170° C. Dewar and Fleming found by means of the low temperature obtained by liquid oxygen that thermoelectric inversion for this pair does occur at about −170°.

5. Electromotive Force in the Thermoelectric Diagram. — From the manner in which a thermoelectric diagram is constructed, it will be seen that the emf between any pair of metals is equal to the area of the figure included between the ordinates corresponding to the two temperatures and the thermoelectric lines of the metals. Thus if the cooler junction of a copper-iron couple be at 100° and the warmer at 200°, the resultant emf in the circuit is represented by the area *abcd;* while if the warmer junction be at 400°, the emf will be equal to the difference of areas *abn* and *c'd'n*.

The ordinates represent thermoelectric powers and

$$dE/dT = \textit{thermoelectric power;}$$

therefore

$$dE = \textit{thermoelectric power} \times dT.$$

Now dE is the small increase of emf corresponding to the small increase of temperature dT, and the second member of the last equation is a small area whose length is the line *ab* and whose width is an element of temperature measured at right angles to *ab*. The emf of any finite temperature difference is therefore an area such as *abcd*, which is made up of small areas corresponding to minute temperature differences.

6. Thermoelectric Series. — A thermoelectric series is a table of metals showing their thermoelectric relation to one another. Since the thermoelectric power depends on the absolute temperature of the junctions, such a list is good only for some definite mean temperature. The following series gives the emf in microvolts (millionths of a volt) between each metal and lead, with a difference of one degree between the junctions when their mean temperature is 20° C.:

Bismuth	− 89.0	Silver	+ 3.0
Cobalt	− 22.0	Zinc	+ 3.7
German silver	− 11.75	Copper	+ 3.8
Mercury	− 0.418	Iron	+ 17.5
Lead	0.0	Antimony, axial	+ 22.6
Tin	+ 0.1	Antimony, equatorial	+ 26.4
Platinum	+ 0.9	Tellurium	+ 502.0
Gold	+ 1.2	Selenium	+ 807.0

When a junction of any pair of these metals is moderately heated, the current flows across it from the metal standing higher in the list toward the one standing lower. For the smaller values of the thermoelectric powers, the results obtained by different observers are not very concordant.

CHAPTER II

HERMO-ELECTROMOTIVE FORCE BETWEEN METALS AND LIQUIDS

7. Introductory. — The laws of thermoelectric force between metals have long been known, and they have been described in the preceding chapter only as a prelude to the study of the second class of thermoelectromotive forces, namely, those between metals and solutions of their salts. These latter have been but little known and only slightly appreciated. And yet they have most interesting applications in electrolysis and in voltaic and concentration cells. They are readily distinguished from the well-known first class because emf arising at the junction of two metals is a function of temperature only, while an emf having its seat at the junction of a metal and a solution of one of its salts is a function not only of temperature but also of *the concentration of the salt solution,* or of *the concentration of the metal in the form of an amalgam.*

It is therefore quite possible to have an emf in circuit, in the absence of any difference of con-

centration at the two electrodes, by reason of a difference of temperature of the two metal-liquid junctions; also, in the absence of any temperature difference, by reason of a difference either in the concentration of the salt solutions bathing the electrodes, or of the amalgams composing them. This latter emf is properly called thermoelectric because the energy of the current in a closed circuit when no other source of emf is present represents the excess of heat absorbed at one electrode above the heat generated at the other during the passage of one coulomb. In the absence of chemical energy and heat of dilution, the heat of the solutions or of the amalgams is the only energy present to be drawn upon.

If this appears to the reader improbable, the writer trusts that he will withhold judgment until he has read and considered the thermodynamic and experimental evidence appearing later in this book.

8. Thermo-electromotive Force between Zinc and Zinc Chloride. — For the purpose of measuring the effect of a change of temperature between the electrode and the electrolyte, a special form of cell was employed. It consisted of two tubes communicating with each other

near their upper ends by a long tube of narrow bore (Fig. 4). All three tubes were filled with a solution of zinc chloride, density 1.395 g. per cm.^{3} at 15° C. Metallic zinc wires were used as the electrodes. One electrode *A* was kept in an ice bath, while the temperature of the other was raised by short steps. The measurement of the emf was made by the potentiometer

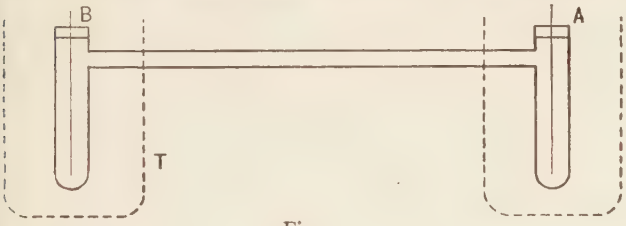


Fig. 4

method, the experimental cell being balanced in series with a Clark standard cell. Thus the closing of the key indicated at a glance which pole of the experimental cell was positive. With zinc in a solution of one of its salts the heating of the electrode always produces an emf *directed from the solution to the metal;* that is, the electrode in *B* was always positive whether the experimental cell contained a solution of zinc chloride or zinc sulphate.

With the combination

$$\text{Zn (warm)} \,|\, \text{ZnCl}_2 \,|\, \text{Zn (cold)}$$

the relation between the emf and the difference of temperature t or $T_2 - T_1$ between the two electrodes is a linear one represented by the equation

$$E = 0.000590\ (T_2 - T_1).$$

In the table the observed and computed emfs are set down for comparison.

Temp.	Obs. emf	Comp. emf	Difference
8.1°	0.00490	0.00478	− 12
10.5°	612	608	− 4
12.3°	750	726	− 24
17.7°	1040	1044	+ 4
22.2°	1301	1310	+ 9
25.8°	1499	1522	+ 23
28.6°	1668	1687	+ 19
32.1°	1913	1894	− 19
34.5°	2050	2036	− 14
39.1°	2295	2307	+ 12

The observations are plotted in the straight line of Fig. 5.

9. Thermo-electromotive Force with Amalgams. — Figure 6 was plotted from the emfs obtained by setting up the two-limbed cell twice, each time with the same zinc amalgam in both limbs. The amalgam was in a half gram-molecule solution of zinc sulphate. One limb was kept in ice at 0°, while the temperature of the other

was raised by steps from 0° to about 32°. The direction of the emf is from the solution to the amalgam across the heated junction. It is greater for the *dilute* amalgam than for the concentrated one. Curve *A* is for the dilute amalgam and curve *B* for the concentrated. These curves are nearly straight lines, and the corre-

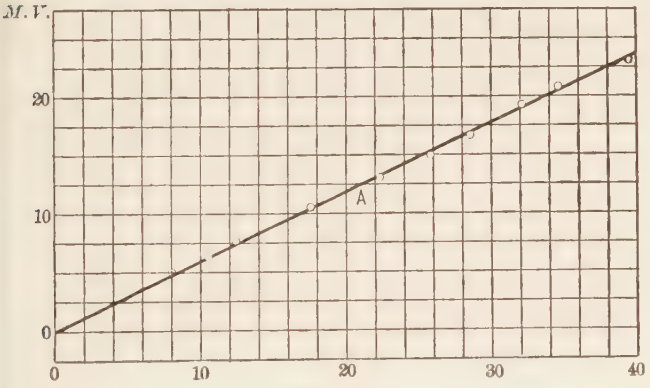


Fig. 5

sponding thermoelectric power is about one millivolt for the dilute and a little less than 0.8 millivolt for the concentrated amalgam. The concentration of the one amalgam was one-tenth that of the other.

Take another case. Two zinc amalgams were made by weighing out masses of mercury as one to two and depositing in them electrically the

same quantity of zinc. The weight of zinc was 0.6 and 1.2 per cent respectively of the weight of mercury. The electrolyte was a concentrated solution of zinc sulphate.

To measure the electrolytic thermo-electro-

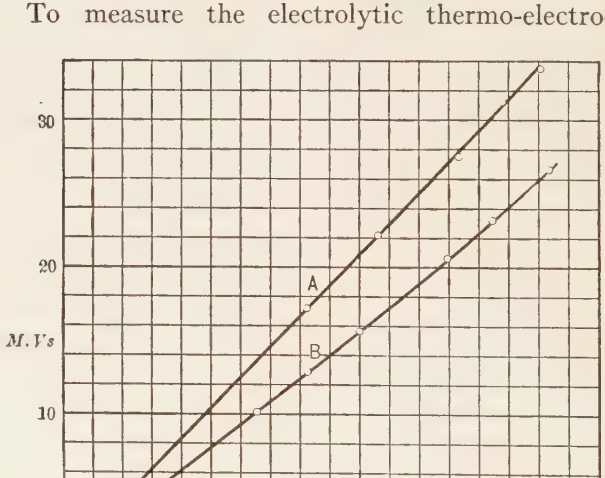


Fig. 6

motive force of the two amalgams, the two legs of the **H**-form of cell, identical in every respect as far as possible, were immersed in baths, one containing mixed ice and water, and the other water, the temperature of which was varied. The entire cell, except the short portion connect-

ing the side tubes, was immersed. The results are the following:

THERMO-ELECTROMOTIVE FORCE FOR THE MORE DILUTE AMALGAM

Temp. C	Obs. emf	Comp. emf
10.30°	0.01077	0.01077
15.40°	1611	1611
20.47°	2140	2141
25.60°	2676	2678
31.10°	3251	3253
36.80°	3852	3849
40.20°	4214	4205

Equation: $E_1 = 0.001046(T_2 - T_1)$.

THERMO-ELECTROMOTIVE FORCE FOR THE MORE CONCENTRATED AMALGAM

Temp. C.	Obs. emf	Comp. emf
9.41°	0.00956	0.00957
14.75°	1496	1500
19.65°	1996	1998
25.05°	2542	2547
30.60°	3110	3112
35.20°	3582	3580
39.30°	4000	3993

Equation: $E_2 = 0.001017(T_2 - T_1)$.

The thermo-electromotive force is directed from the solution to the amalgam, and it increases as the *dilution* of the amalgam increases. In other

words, the electrolytic thermo-electromotive force is a function of the concentration as well as of the temperature.

The two curves in Fig. 7 represent the observations for E_1 and E_2 respectively.

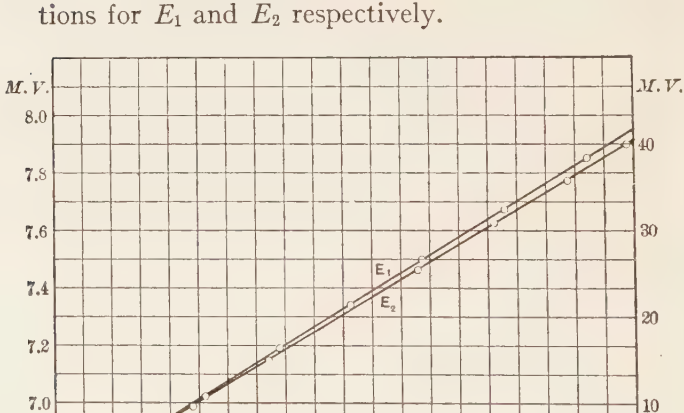


Fig. 7

10. Thermoelectric Behavior of Silver.[1] — In a thermoelectric element of a metal and a solution of one of its salts, in the case of zinc, copper, cadmium, and mercury, the warm electrode is the cathode, but in the case of silver the cold electrode is the cathode, that is, the thermo-emf is directed from the metal to the solution.

[1] Henderson, Phys. Rev., Vol. XXIII, Aug., 1906.

The tests show that this is not due to oxidation or other peculiarity of the electrode. Cells, from which the air had been carefully removed, gave the same result, both in direction and magnitude.

Further, an increase in concentration of the solution produces a decrease in the thermo-emf. The maximum decrease occurs between one-eightieth and one-tenth normal solution. In a simple concentration cell with silver electrodes, on the concentrated side the emf is smaller than on the dilute side. Hence within the cell the current flows from the electrode in the dilute solution to that in the concentrated solution. Thus silver goes into solution at the anode and increases the concentration there, while at the cathode silver goes out of solution and is deposited on the cathode, thus reducing the concentration there. As in the other cases, then, the passage of the current tends to reduce the difference of concentration, or the cell runs down.

CHAPTER III

CONCENTRATION CELLS

11. Concentration Cells of Two Types. — Two types or classes of concentration cells should be distinguished from each other:

1. Two electrodes of the same metal immersed in a solution of a salt of this metal, the concentration of the solutions being different at the two electrodes.

2. Two electrodes consisting of an amalgam of the same metal, both immersed in a solution of a salt of the metal, the concentration of the amalgams being different at the two electrodes.

When all sources of emf are taken into account, the formula for the first type worked out on the solution pressure and osmotic pressure, or Nernst theory, is as follows:

$$E = -0.0002\frac{i}{n}\cdot\frac{v}{u+v}T\log\frac{c_1}{c_2}.$$

Here i is the Van't Hoff factor of dissociation, u and v the ionic velocities of the positive and negative ions respectively, and c_1 and c_2 the con-

centration of the solutions; n is the valence of the metal ion. Lüpke says of this formula: "The minus sign in the above formula means that within the concentration cell the current goes from the dilute to the concentrated solution, so that the electrode in the latter is the cathode and in the former the anode."

It will be observed that by this formula the emf is proportional to the absolute temperature T of the cell. This suggests that the emf of such a cell is thermal in origin; in other words, that concentration cells are devices for converting some of the heat of the solutions and surroundings into electric energy.

We shall arrive at the same conclusion if we consider the Helmholtz equation for the emf of a voltaic cell,

$$E = \frac{H}{nF} + T\frac{dE}{dT},$$

where H is either the heat equivalent of the chemical reactions or the heat of dilution in the cell.

If the Helmholtz equation is generally applicable, it follows that when H is zero, the only source of electrical energy is the heat of the cell and its surroundings represented by the second term. Usually H has either a positive or a negative value arising from the heat of dilu-

tion of the solutions of different concentration. Obviously the emf of a concentration cell is at least in part thermoelectric, and it remains to apply the principles of electrolytic thermo-electromotive force to concentration cells.

12. Relation between Thermo-EMF and Concentration. — Figure 8 shows the results of

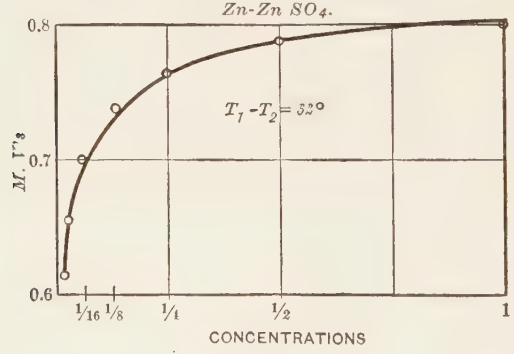


Fig. 8

the determination of thermo-emf per degree C. for Zn–$ZnSO_4$ with concentrations ranging from 1/100 gram-molecule to one gram-molecule to the liter. The ordinates express the results in millivolts per degree C., the temperature of the two sides being 0° and about 30°. The measurements were made by means of a cell similar to the one shown in Fig. 4. One limb was kept in a bath of ice-cold water, and the other in a

bath of water at about 30°. A series of six such cells were placed in the same baths and were filled with solutions of different concentration of the same salt solution. The two zinc electrodes were moved along from one cell to the

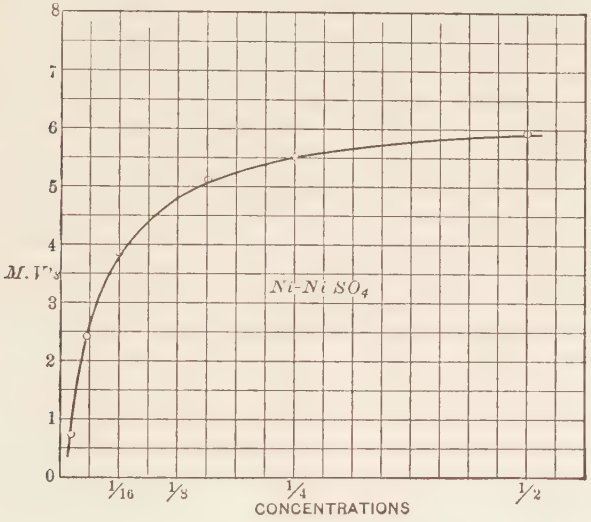


Fig. 9

next, measurement being made in each case twice, the electrodes having been exchanged between the two series for the purpose of eliminating any chance difference between them.

The result is that the emf between zinc and zinc sulphate increases with the concentration

of the sulution. The same law is illustrated by Fig. 9 in the case of nickel and nickel sulphate. In the latter case the increase of thermo-emf with concentration is very much greater than with zinc and zinc sulphate.

13. Electromotive Force Due to a Difference in Concentration. — Figure 10 is a diagrammatic sketch of a Zn–$ZnSO_4$ concentration cell. The small arrows show the direction of the thermo-emfs between the two solutions and the zinc electrodes. Since the thermo-emf on the concentrated side is greater than that on the dilute side, the difference is in favor of the greater concentration and therefore the zinc in the concentrated solution is the cathode, as shown by the long curved arrow on top. If a current is permitted to flow, zinc goes into solution at the anode and increases the concentration of the solution there, while at the cathode zinc is deposited on the electrode and the concentration decreases. The action of the cell is thus to reduce the difference of concentration at the two electrodes.

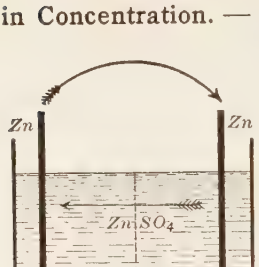


Fig. 10

14. EMF Due to Concentration of Amalgams. — It will be remembered that the thermo-emf in the case of amalgams increases as the amalgam becomes more dilute. Figure 11 is a sketch of a two-legged cell set up with amalgams of different concentrations. The direction of the emf at the contact of solution and amalgam is from the former to the latter, while the greater emf in this case is on the side of the dilute amalgam.

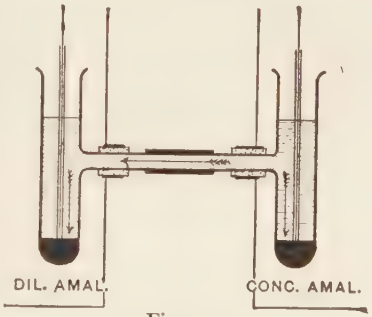


Fig. 11

Thus the dilute amalgam is the cathode. At the anode the metal from the amalgam goes into solution when the cell functions and at the cathode metal is deposited on the amalgam and unites with it. The result is that the passage of the current reduces the difference in concentration; also less heat is liberated at the anode than is absorbed at the cathode. The difference becomes electric energy. The heat of dilution of the amalgams is represented by H in the Helmholtz formula. This also adds its quota algebraically to the emf.

A concentration cell composed of cadmium amalgams and cadmium sulphate has an emf following the linear relation. The two amalgams had concentrations of approximately 2 per cent and 0.783 per cent. The following are the

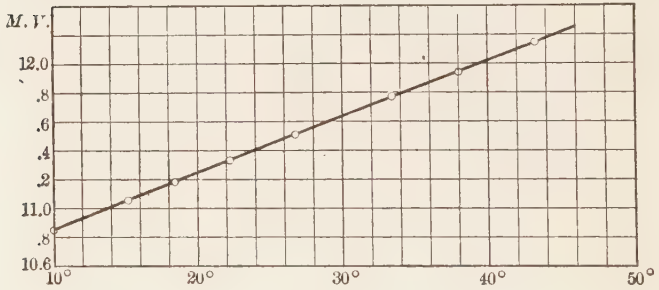


Fig. 12

measured emfs compared with those computed by the equation

$$E = -0.000219 + 0.00003915\ T:$$

Temp.	Obs. emf	Comp. emf	Per cent difference
10.05°	0.010862	0.010862	0.0
15.10°	11063	11060	− .03
18.42°	11190	11190	.0
22.10°	11336	11334	− .02
26.80°	11517	11518	+ .01
33.40°	11773	11776	+ .03
38.00°	11942	11956	+ .12
43.20°	12160	12160	0.0

The heat of dilution comes out a small negative quantity of -10 calories per gram-molecule of cadmium. The observations are plotted in Fig. 12, the straight line representing the equation for E.

The measurements of Richards and Wilson

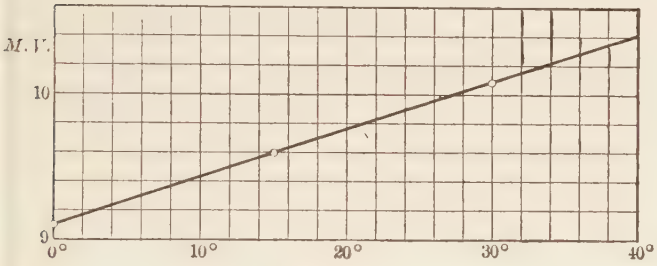


Fig. 13

on a concentration cell of thallium amalgams are also in point.[1] These measurements were made with extreme care to prevent oxidation at three temperatures, 0°, 15° and 30° C. The per cents of thallium in the two amalgams were 0.2294 and 0.1575 in the case chosen for plotting in Fig. 13. The relation between emf and temperature is closely linear.

[1] Carnegie Institution of Washington, Publication No. 118, p. 22.

CHAPTER IV

TEMPERATURE COEFFICIENTS

15. The Temperature Coefficient of a Voltaic Cell. — The effect of a change of temperature on the emf of a voltaic cell is made up of the several temperature effects, and it may be determined as a whole or by synthesis out of its component parts. The whole effect is the algebraic sum of the several thermo-emfs in the internal circuit of the cell. The first attempt at the analysis of the temperature coefficient of a voltaic cell appears to have been made by Bouty.[1] Bouty's measurements were made by a Lippmann voltmeter and lacked modern accuracy. In fact so imperfect were they that he failed to find any relation between thermo-emf and concentration. He says: "I have ascertained that between very wide limits it is independent of the concentration of the liquid." Hence the paper has little value except from an historical point of view.

[1] Jour. de Phys., 1880, p. 229.

Since both zinc and copper, each in a solution of its sulphate, tend, when heated, to play the rôle of copper in a simple voltaic cell, it is evident that they must exhibit the same phenomenon when set up together as a Daniell cell. When the entire cell is heated, the emf tends to rise because of the thermo-emf at the copper electrode, while the zinc and its sulphate produce at the other junction a counter emf. Whether or not the emf of the cell as a whole will rise or fall depends on the relative values of the two thermoelectric powers. A little consideration will show that if the $Cu–CuSO_4$ side alone of a Daniell cell is heated, the emf of the cell will increase, while heating the $Zn–ZnSO_4$ side alone will cause a decrease of emf somewhat greater than the former rise. This conclusion was fully justified by the writer nearly thirty years ago. The changes of emf resulting from heating the copper side were positive, and from heating the other negative. Both are plotted as positive ordinates in Fig. 14 in order the better to compare them and to exhibit the difference. Curve *A* belongs to zinc and curve *B* to copper. The difference between the two thermoelectric powers was 0.00014. Measurements made with separate cells set up with $Zn–ZnSO_4$ and $Cu–CuSO_4$ gave

a difference of 0.00006, which is very near the change in voltage per degree obtained from a Daniell cell, namely, − 0.000073. The change in emf per degree for a Daniell cell is negative and very small.

The data in the table are those used in plotting Fig. 14:

Temp. $Zn-ZnSO_4$	Temp. $Cu-CuSO_4$	Corrected temp. dif.	Change of emf in volts	EMF per deg. C.
1.0	0.9	0.1		
10.8	0.8	9.9	0.00612	0.00062
18.8	0.9	17.8	0.01115	0.00063
29.6	1.2	28.3	0.01884	0.00067
45.9	1.3	47.5	0.03548	0.00075
1.5	1.8	0.3	.....	.....
1.4	15.2	13.5	0.00722	0.00053
1.4	26.4	24.7	0.01382	0.00056
2.0	38.8	36.5	0.02182	0.00060
1.4	40.0	38.3	0.02277	0.00059
1.3	48.5	46.9	0.02842	0.00061

In the Daniell cell there is a third junction, the one between the two sulphates on opposite sides of the cell. Is this thermo-emf negligible?

To investigate this last question, an experimental cell was made in which the connecting tube was curved so as to include a long U, and

the junction of the two sulphates was at the bottom of this U when the cell was set up as a Daniell. After balancing in the usual manner, the U-tube was placed in a hot water bath, by which its temperature was raised from 17° to

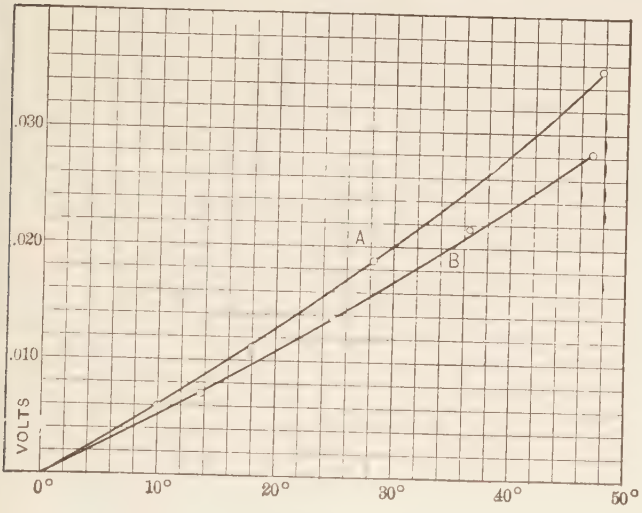


Fig. 14

52°, or through a range of 35° C. No effect was produced upon the emf of the cell; or if any, it was less than one ten-thousandth of a volt for the entire range of 35°.

16. Thermoelectric Power of Zinc–Zinc Sulphate. — The measurements were made by the potentiometer method as arranged by Lord

Rayleigh many years ago. The emf was not read off directly, but was found in terms of the drop of potential over a resistance to balance.

The experimental cell, set up with amalgamated zinc wires in a solution of zinc sulphate,

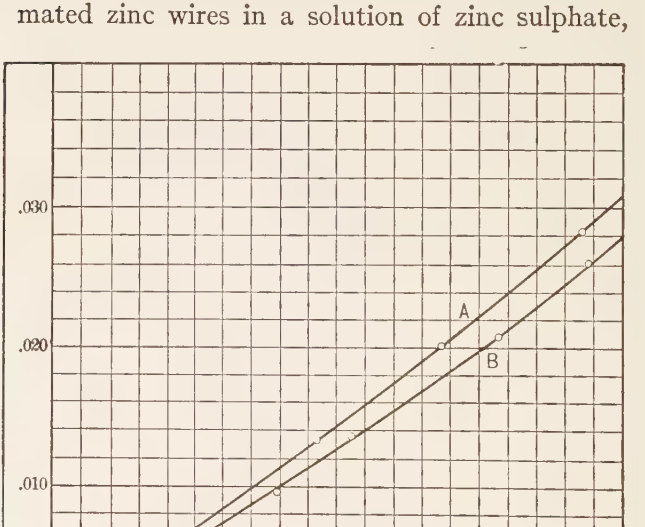


Fig. 15

was immersed with its two legs in separate baths. One was kept at a temperature near zero, while the temperature of the other was raised step by step with stirring of the bath, and the ther-

mometer was read coincidently with the establishment of a balance. The emf is directed from the liquid toward the electrode.

The table contains the data for one set of experiments. There was reason to believe that the observation marked doubtful, included an error in making the balance on the potentiometer. The thermoelectric power at a mean temperature of about 19° is 0.00076. Curve *A* of Fig. 15 is for the $Zn–ZnSO_4$.

Temp. C. left limb	Temp. C. right limb	Temp. difference (corrected)	Change in emf in volts	EMF per degree C.
0.6	0.4	0.2	.....	.....
9.8	0.4	9.2	0.00660	0.00072
14.4	0.4	13.8	0.00911?	0.00065?
19.0	0.4	18.4	0.01319	0.00720
27.8	0.4	27.2	0.02011	0.00074
37.6	0.4	37.0	0.02812	0.00076

17. Thermoelectric Power of Copper–Copper Sulphate. — The apparatus was set up in precisely the same manner as before, with a solution of chemically pure copper sulphate of density 1.11. Two freshly electroplated copper wires were used as electrodes to dip with the thermometers into the solution. The current produced on heating one limb was found to have

the same direction as in the case of zinc sulphate, viz. from the cold limb to the warm through the liquid. The copper in the cold acts like the zinc of a simple voltaic cell. The following table contains all the data:

Temp. C. left limb	Temp. C. right limb	Temp. difference (corrected)	Change in emf in volts	EMF per degree C.
0.6	0.4	0.2	.....	.....
5.1	0.4	4.5	0.00252	0.00056
9.6	0.4	9.0	0.00582	0.00065
16.1	0.2	15.7	0.00944	0.00060
21.7	0.6	20.9	0.01369	0.00066
32.1	0.5	31.4	0.02061	0.00066
38.4	0.5	37.7	0.02611	0.00069

The thermoelectric power for the copper–copper sulphate couple is therefore 0.00069 for the mean temperature of 19°. The total emfs in volts, due to heating one limb, are plotted as ordinates, and the difference of temperatures as abscissae. Curve *B* in Fig. 15 refers to copper and copper sulphate. It will be noticed that both curves are slightly concave upwards, indicating probably some oxidation of the electrodes as the temperature rises.

18. Temperature Coefficient of a Daniell Cell. — A comparison of the thermoelectric powers

of the last two tables shows that the resultant effect upon the emf of a Daniell cell, due to the heating of the cell as a whole, should be the difference of the two thermoelectric powers of $Zn–ZnSO_4$ and $Cu–CuSO_4$, or $0.00076 - 0.00069$, or 0.00007. The thermoelectric power of each electrode in a solution of its sulphate is independent of the temperature of the other electrode. Thus the change in the emf of the cell per degree must be the difference between the two thermoelectric powers, since one lowers this emf and the other raises it.

Many difficulties have always been encountered in measuring the change in emf per degree in the case of a Daniell cell. The chief difficulty is occasioned by oxidation of the electrodes. Oxidation of the copper electrode raises the emf, while oxidation of the zinc electrode lowers it. In the most carefully conducted determination the mean value of the fall of emf per degree was found to be 0.000073. This is substantially the same as the difference of the two thermoelectric powers. The effect of a change of temperature on the Daniell cell is practically negligible. It is smaller than known disturbances assignable to other causes particularly to the effect of oxidation.

19. Thermoelectric Power of Mercury–Mercurous Sulphate. — Chemically pure mercury was placed in each branch of the experimental cell and on this was placed neutral mercurous sulphate. Both branches and the thin connecting tube were filled with a neutral solution of zinc sulphate saturated at 0°. Connection was made with the mercury in each limb by sealing a long platinum wire into a glass tube, leaving a short portion of the wire exposed at the sealed end. This was pushed down into the mercury on either side. One limb of the cell was then immersed in melting snow, while the other was heated step by step with the results shown in the table.

Temp. left limb	Temp. right limb	Temp. difference	EMF in volts	EMF per degree C.
0°	0°	0°	.....	.....
8.30	0	8.30	0.00173	0.00021
14.50	0	14.50	0.00314	0.00022
20.70	0	20.70	0.00456	0.00022
26.70	0	26.70	0.00605	0.00023
35.80	0	35.80	0.00833	0.00023

In Fig. 16 the results are plotted in the curve *B*, together with those derived from zinc–zinc sulphate, curve *A*. These measurements include

the effect of the contact of the platinum with mercury, as well as that of $ZnSO_4$ and Hg_2SO_4. But these are purposely included with a view of analyzing the temperature coefficient of the Clark cell.

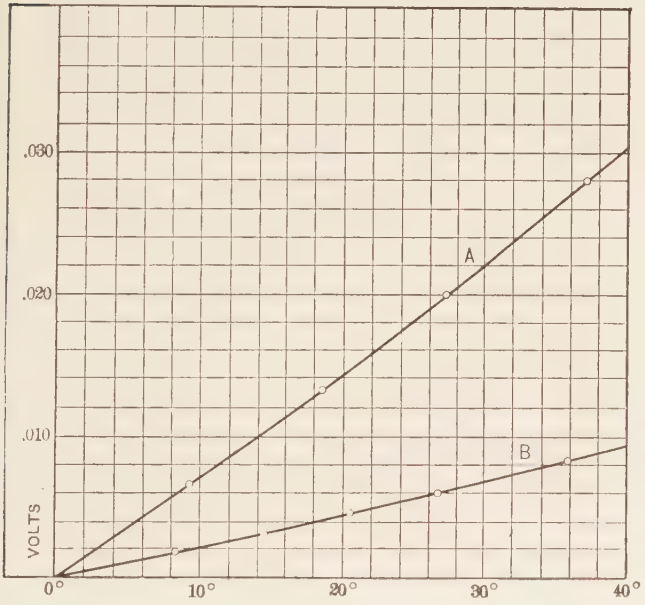


Fig. 16

The effect of heating the positive or mercury electrode is added to the whole emf of the cell, while that at the negative or zinc electrode is opposed to the emf of the cell, and must be subtracted. The algebraic result is, then, the dif-

ference of the two thermoelectric powers, and is negative because that for the $Zn–ZnSO_4$ is larger than the other. The difference is 0.00076 less 0.00023, or 0.00053. A long series of measurements made on a cell set up with these same solutions was 0.00056 per degree C.

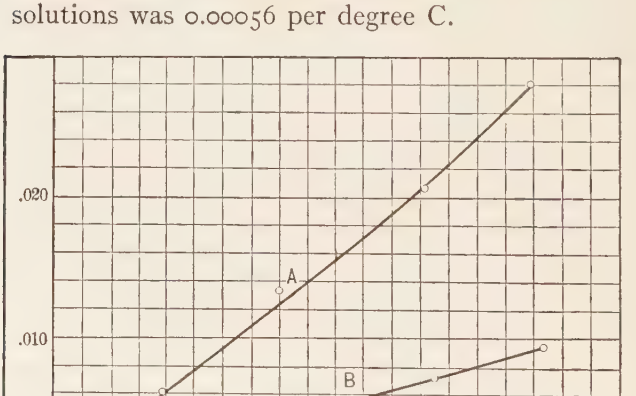


Fig. 17

20. The Experimental Cell as a Clark Cell. — By simply substituting an amalgamated zinc wire, dipping into the zinc sulphate solution, for the platinum wire of the last experiment, the experimental cell becomes a Clark standard cell. Heating the mercury side alone increases the emf of the cell; heating the zinc side alone lowers

the emf. The results of the measurements are placed in the table and are plotted in Fig. 17.

Temp. $Zn + ZnSO_4$	Temp. Hg_2SO_4	Temp. difference	Difference in volts	EMF per degree
15.75	15.8	0.05	....	....
15.80	23.6	7.80	0.00189	0.00024
16.00	34.2	18.20	0.00472	0.00026
16.20	43.2	27.00	0.00708	0.00026
16.25	50.7	34.45	0.00944	0.00027
16.25	15.7	0.55	....	....
23.25	15.7	7.55	0.00598	0.00079
31.60	15.7	15.90	0.01298	0.00082
40.00	15.7	24.30	0.01872	0.00077
49.40	15.7	33.70	0.02800	0.00083

The difference between the two mean thermo-electric powers is $0.00083 - 0.00027 = 0.00056$ as compared with 0.00053 of the last article. This is the same value as the one obtained by heating the cell as a whole. The formula for the emf of this cell is then

$$E_t = E_{15} - 0.00056(t - 15).$$

A wide range of temperature requires for accuracy another term $+ 0.0000007(t - 15)^2$. The change in emf for one degree C. is the following linear function of the temperature:

$$- 0.00056 + 0.0000014(t - 15).$$

21. $\frac{dE}{dT}$ for the Calomel Cell. — The scheme of the well-known calomel cell is

$$Zn \mid ZnCl_2 \mid HgCl \mid Hg$$

The thermo-electromotive force of the zinc side of this cell has already been described in Article 8. The results are represented by a straight line the equation for which is

A. $$E = 0.000590\, t.$$

Since one side of the cell was kept at 0° C., the difference of temperature is denoted by the reading of the centigrade scale.

The mercury electrode was then subjected to the same treatment with the following results:

B. $Hg \mid HgCl \mid ZnCl_2 \mid HgCl \mid Hg$

Temp.	Obs. emf	Comp. emf	Difference
7.1°	0.00517	0.00486	− 31
10.6°	730	726	− 4
12.9°	882	884	+ 2
16.5°	1125	1130	+ 5
19.8°	1358	1356	− 2
22.8°	1561	1562	+ 1
25.3°	1729	1733	+ 4
27.9°	1928	1911	− 17
31.8°	2170	2178	+ 8
34.1°	2340	2336	− 4
36.8°	2554	2521	− 33

For A, $E_1 = 0.000590\,t$; for B, $E_2 = 0.000685\,t$. Whence for this calomel cell

$$\frac{dE}{dT} = \frac{E_2 - E_1}{t} = 0.000095.$$

The following table shows the observed emfs compared with those computed from the equation

$$E = 1.0005 + 0.000095\,(t - 15^\circ)$$

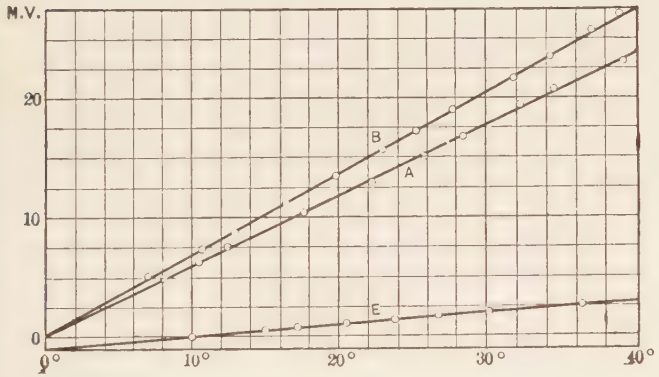


Fig. 18

up to about 35°; for higher temperatures the observed values exceed the computed ones, perhaps because of the increased solubility of the calomel at those temperatures.

The results are plotted in Fig. 18. The inclined line at the bottom marked E is drawn from the above equation and passes through

9.75°, where the emf of the cell is 1 volt. The observed emfs are plotted along this line, on another scale.

Temp.	Obs. emf	Comp. emf
10.0°	1.0001	1.00003
15.0°	1.0005	1.00050
17.2°	1.0007	1.00071
20.4°	1.0010	1.00101
23.7°	1.0013	1.00133
26.7°	1.0016	1.00161
30.2°	1.0020	1.00194
36.4°	1.0025	1.00253

CHAPTER V

THERMODYNAMICS OF THE VOLTAIC CELL

22. The Reversible Voltaic Cell. — The theory commonly known as that of Thomson (Lord Kelvin) that the electrical energy of a reversible voltaic cell is the equivalent of the chemical energy transformed has been abandoned as an exact expression of the facts, since the appearance of Helmholtz's paper on "Die Thermodynamik Chemischer Vorgänge,"[1] followed by the experimental corroboration of Jahn[2] and others. It is now well understood that the electrical energy output of a reversible cell may be either greater or less than the heat equivalent of the chemical reactions. It is greater when the temperature coefficient of the cell is positive, and it is less when it is negative. If such a cell is connected in a circuit with an external resistance so large in comparison with the internal resistance of the cell that the Joule's heat due to the internal resistance is vanishingly small, then heat

[1] Sitzungsber. der Akad. der Wiss. zu Berlin, I, 1882, p. 24.
[2] Wied. Ann., Vol. XXVIII, pp. 21 and 491, 1886.

must be added to the cell to keep its temperature constant when a current passes through it if its temperature coefficient is positive. On the contrary, if its temperature coefficient is negative, it must give up heat to surrounding bodies to remain in thermal equilibrium. In the former case all the potential energy transformed goes over into electrical energy, and in addition some heat undergoes a similar transformation. In the latter case, only a part of the transformed chemical energy becomes electrical in form; the remainder appears as heat. The calomel cell devised by Helmholtz is an example of a cell with a positive temperature coefficient and a converter of heat into electrical energy. The Clark standard cell, on the other hand, has a negative coefficient and gives up heat or grows warmer when it furnishes current as a primary cell. In the Daniell cell the electrical energy is almost the exact equivalent of the difference between the heat of combination of the zinc sulphate formed and of the copper sulphate decomposed. It was long ago noticed by Poggendorff that the Daniell element enjoys, when it is heated, an almost complete invariability, despite the variation of electromotive forces at the two surfaces of contact, copper–sulphate of cop-

per and zinc–sulphate of zinc. These variations, equal in absolute value, act in a contrary sense and produce equilibrium.[1]

23. Thermodynamics of a Voltaic Cell. — The Helmholtz principle has heretofore been applied to a voltaic cell in bulk, as it were. In the investigation about to be described it is applied to the cell in parts — that is, the positive and negative sides are treated separately in order to bring out clearly the rôle played by the thermo-emf on the two sides of the cell. In other words, the thermodynamics of a voltaic cell is considered more in detail than has hitherto been done. The treatment is an extension of the Helmholtz principle.

A reversible cell is one of which it is at least theoretically true that the electrical energy obtained from its action, when applied inversely so as to reverse the chemical operations, exactly suffices to restore the cell to its initial condition. Imagine the electromotive force of a Daniell cell compensated by a second inverse electromotive force. If the latter is reduced, a current passes through the Daniell cell in the normal direction, zinc goes into solution and copper is deposited. If the opposing electromotive force

[1] Pogg. Ann., t. L, p. 264, 1840

is made to exceed that of the Daniell, copper goes into solution and zinc is deposited. When equal quantities of electricity have passed in the two directions, the cell has been restored to its initial condition and the cycle is complete. Hence the laws of thermodynamics may be applied to such a reversible process.

24. Application of Thermodynamics. — Let T be the temperature on the absolute scale and dH the quantity of heat which must be applied to the cell or be taken from it in order to keep its temperature constant during the passage of a quantity of electricity dq, exclusive of the Joule's heat. Also let u be the total energy contained in the cell. It is a function of the temperature of both the positive and negative sides of the cell, the cell being constructed so that its two sides may be separately considered. It is also a function of the quantity of electricity q passing through the cell.

Then from the principle of the conservation of energy (indicating the positive side of the cell by the subscript p and the negative by subscript n, and letting E denote the electromotive force),

$$J \cdot dH = \left(\frac{\partial u}{\partial T}\right)_p dT + \left(\frac{\partial u}{\partial T}\right)_n dT + \left[\frac{\partial u}{\partial q} + E\right] dq \,. \quad (1)$$

The change of entropy dS during the flow of dq is

$$dS = J\frac{dH}{T} = \frac{1}{T}\left[\left(\frac{\partial u}{\partial T}\right)_p dT + \left(\frac{\partial u}{\partial T}\right)_n dT\right] + \frac{1}{T}\left[\frac{\partial u}{\partial q} + E\right]dq \quad \ldots\ldots (2)$$

Hence

$$\frac{\partial S}{\partial T} = \frac{1}{T}\left[\left(\frac{\partial u}{\partial T}\right)_p dT + \left(\frac{\partial u}{\partial T}\right)_n dT\right]$$

and

$$\frac{\partial S}{\partial q} = \frac{1}{T}\left[\frac{\partial u}{\partial q} + E\right] \quad \ldots\ldots\ldots\ldots\ldots (3)$$

Differentiating the first of equations (3) with respect to q and the second with respect to T,

$$\frac{\partial^2 S}{\partial T \cdot \partial q} = \frac{1}{T}\left[\left(\frac{\partial^2 u}{\partial T \cdot \partial q}\right)_p + \left(\frac{\partial^2 u}{\partial T \cdot \partial q}\right)_n\right]$$

$$= \frac{1}{T}\left[\left(\frac{\partial^2 u}{\partial T \cdot \partial q}\right)_p + \left(\frac{\partial^2 u}{\partial T \cdot \partial q}\right)_n + \left(\frac{\partial E}{\partial T}\right)_p + \left(\frac{\partial E}{\partial T}\right)_n\right] - \left[\frac{\partial u}{\partial q} + E\right]\frac{1}{T^2}$$

or

$$T\left[\left(\frac{\partial E}{\partial T}\right)_p + \left(\frac{\partial E}{\partial T}\right)_n\right] = \frac{\partial u}{\partial q} + E \quad \ldots\ldots (4)$$

Substituting in equation (1),

$$J \cdot dH = \left(\frac{\partial u}{\partial T}\right)_p dT + \left(\frac{\partial u}{\partial T}\right)_n dT + T\left[\left(\frac{\partial E}{\partial T}\right)_p + \left(\frac{\partial E}{\partial T}\right)_n\right]dq \quad \ldots\ldots\ldots\ldots (5)$$

This last equation is the heat, expressed mechanically, which must be added to the cell or abstracted from it to keep its temperature constant while the quantity of electricity dq is passing through it. In fact, if dT is zero, the equation becomes

$$J \cdot dH = T\left[\left(\frac{\partial E}{\partial T}\right)_p + \left(\frac{\partial E}{\partial T}\right)_n\right] dq \ldots\ldots (6)$$

$T\left(\frac{\partial E}{\partial T}\right)_p$ is the temperature coefficient of the positive side of the cell, the temperature of the negative side remaining constant; $T\left(\frac{\partial E}{\partial T}\right)_n$ is the temperature coefficient of the negative side, the temperature of the positive side being maintained constant; the whole bracketed quantity times T is the temperature coefficient of the cell as a whole, neglecting any small coefficient due to the thermo-emf at the junction of the two halves of the cell.

The positive and negative coefficients are the thermo-emfs at the contacts between the two electrodes and the liquids bathing them respectively. Still neglecting the thermo-emf at the junction between the two sides of the cell, the temperature coefficient of the entire cell is zero only when

$$\left(\frac{\partial E}{\partial T}\right)_p + \left(\frac{\partial E}{\partial T}\right)_n = 0,$$

that is, when the coefficients on the two sides are numerically equal and of opposite sign; or else when both are zero. The first condition is nearly realized in the Daniell cell. For $\underset{\leftarrow}{Cu}-CuSO_4$, $\left(\frac{\partial E}{\partial T}\right)_p$ is 0.00074 for a range of temperature of 5.6° near 19°. For $\underset{\leftarrow}{Zn}-ZnSO_4$ it is 0.00079 for a range of temperature of 8.8° near 23°. The direction of the thermo-emf in both cases is from the liquid to the metal across the heated contact. Hence the former gives the cell a positive temperature coefficient, and the latter a negative one, while the coefficient of the cell as a whole is negative and small (Article 17).

A further consideration of equation (6) shows that the maintenance of a constant temperature on both sides of the cell during the flow of the quantity dq, requires that heat represented in mechanical measure, $T\left(\frac{\partial E}{\partial T}\right)_p dq$, must be *added* to the positive side of the cell, and that a quantity $T\left(\frac{\partial E}{\partial T}\right)_n dq$ must be *withdrawn* from the negative side; or, in other words, these expres-

sions represent the loss of heat on the positive side, and the gain on the negative respectively. Divide them by the thermal capacity respectively of the two sides of the cell, and we have the *fall* of temperature on the positive side and the *rise* on the negative. The sum of the two is then the difference of temperature established between the two sides if no heat passes between them. These temperature changes are due to the thermal or Peltier electromotive force at the two metal-liquid contacts. On the negative side of the Daniell cell, for example, the current from the zinc to the liquid flows against the Peltier electromotive force, and heat is generated. On the opposite side the current flows from the liquid to the copper, or with the Peltier electromotive force at the contact, and therefore heat is absorbed and converted into the energy of the current.

If a reverse current be sent through the cell, all the physical phenomena, except that of the Joule's heat, are reversed. The current on the positive side flows from the copper to the liquid, or against the thermo-emf, and Peltier heat is generated. On the zinc side heat is absorbed. With a reverse current, therefore, the temperature of the positive side of the cell rises faster

than that of the negative, while with a direct current the temperature of the negative side rises faster than that of the positive, that is, under practical conditions where Joule's heat causes a rise of the temperature of the entire cell.

While equation (6) is perfectly general, the preceding conclusions are applicable only when the Peltier electromotive force at the contact of the electrode and the liquid is directed from the latter to the former across the junction, both on the positive and the negative side of the cell. There are some exceptions to this general rule. For example, the thermo-emf of $Fe - FeSO_4$ is zero.[1] Hence a cell consisting of $Fe - FeSO_4 - CuSO_4 - Cu$ has a positive temperature coefficient due to the thermo-emf on the copper side alone of the cell, and the Peltier phenomenon is confined to the positive side of the cell. In the case of the voltaic series $Ni - NiSO_4 - CuSO_4 - Cu$ the two thermo-emfs are in the same direction through the cell. The temperature coefficient is therefore large — about 0.8 per cent per degree — and heat is absorbed at both electrodes. Such a cell takes heat from the surroundings on both sides and converts it into electrical energy.

[1] Am. Jour. Sci., Vol. XLVI, p. 64.

25. Experimental Verification. — The general conclusions arrived at are not difficult to confirm qualitatively. But when quantitative determinations are attempted, serious difficulties are encountered. These may be overcome and the results are highly interesting.

The Daniell cell was chosen because the necessary constants are known with a fair degree of accuracy.

The cell was made as follows: Two glass tubes 9.5 cm. long and 3 cm. in diameter were provided with side tubes near the bottom 18 mm. long and 18 mm. wide (Fig. 19). Heavy tight-fitting rubber collars served to connect the two halves of the cell, with a plate of fine unglazed porcelain between them as shown. The edges of the porcelain were covered with paraffin after the rubber collars had been bound together with fine iron wire. No difficulty was found in making a water-tight joint.

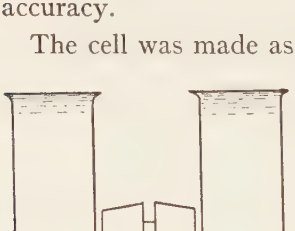


Fig. 19

In most experiments 10 per cent water-free solutions of zinc and copper sulphates were used.

These solutions have relative conductances of 321 and 320.[1] They were chosen with the object of eliminating as far as possible the inequality of Joule's heat between the two sides of the cell. In every experiment 40 cm.^{3} of each solution were placed in the double cell, which was supported by a stout cord in a large pasteboard box and completely surrounded and covered with eiderdown.

The earlier observations were made with two Haak thermometers reading directly to fifths, and by means of a telescope to hundredths of a degree. The copper and zinc plates were attached directly to the thermometers by rubber bands, and the liquids were stirred before taking observations by moving the thermometers and the attached plates from side to side. Since the internal resistance of the cell was over 100 ohms, it was necessary to put it in series with a few storage cells and some resistance, with the double object of varying the current and of causing a reverse current to travel the experimental cell.

The current was measured as follows: The electromotive force of a Weston standard cell

[1] Kohlrausch u. Holborn, Leitvermögen der Elektrolyte, p. 151.

was balanced against a fall of potential over a portion of two resistance boxes containing 10,000 ohms each and joined in series with a storage cell. By means of an appropriate switch consisting of mercury cups in a plate of paraffin, this potential drop was balanced against the fall of potential over the requisite number of ohms in the main circuit. For example, for 0.03 ampere the fall of potential over 34 ohms was thus balanced indirectly against the electromotive force of the Weston cell, which was very nearly 1.02 volts. The current was not allowed to vary more than about 0.05 per cent.

Figure 20 shows the results obtained with a current of 0.02 ampere. Curve I, I, I, belongs to the zinc sulphate and II, II, II, to the copper sulphate, both of which were fifteen per cent solutions. These curves are valuable chiefly because they exhibit two facts rather strikingly. The current through the cell was reversed at the points indicated by the vertical dotted lines. In the first place it is evident that the temperature always rises most rapidly on the side of the cell by which the current enters. The same fact appears in every case and in every trial. In the second place the curves show how the phenomenon is complicated by the change in con-

centration. For this reason the difference in temperature between the two sides of the cell is less before reversal than it would otherwise be, for the concentration and conductance of the zinc sulphate increase while those of the copper sulphate decrease. After reversal this change in

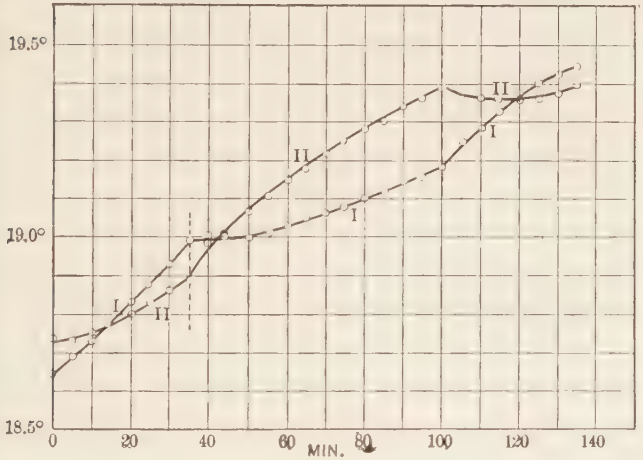


Fig. 20

concentration accelerates the rise of temperature on the copper side and retards it on the zinc side. After reversing the current, an established difference of temperature is reduced to zero in about half the time necessary to produce it. It is therefore obvious that some method had to be devised to eliminate the effect of the change of

concentration as well as that of any difference in resistance on the two sides owing to the dimensions of the apparatus, position of the plates, etc., if reliable quantitative results were to be obtained. For this purpose the following expedients were adopted: First, ten per cent solutions of practically equal specific conductances were used. Second, the duration of any series of observations in either direction was taken inversely as the current, so that the same quantity of electricity was always transferred with the same changes in concentration. This quantity was 72 coulombs — 0.03 ampere for 40 min., 0.04 ampere for 30 min., etc.

Third, a curve was constructed from observations showing the equalization of any established difference of temperature between the two sides of the cell as a function of the time. This may be called for convenience a "cooling curve." By means of this curve it is not difficult to correct any series of observations so as to obtain the temperature differences which would have been observed if heat had not flowed from one side to the other during the time covered by the series. Fourth, to eliminate the effect of the change of concentration and the lack of equal resistance on the two sides, a series of observa-

tions was first taken with a direct current through the cell, and then after reducing the temperature difference again to about zero, *without any current*, another series of equal duration was taken with the current through the cell reversed. After correcting both series by the "cooling curve," the half sum of the two maximum differences was taken as the desired value.

The difference between the heats generated on the positive and negative sides, with the current first direct and then reversed, may be expressed by the two following equations (R' being the resistance of the zinc side and R'' that of the copper):

$$J \cdot \Pi' = I^2R't - I^2dR''t + T\left(\frac{\partial E}{\partial T}\right)_n It - \left[I^2R''t + I^2dR''t - T\left(\frac{\partial E}{\partial T}\right)_p It\right]$$

$$J \cdot \Pi'' = I^2R''t + I^2dR''t + T\left(\frac{\partial E}{\partial T}\right)_p It - \left[I^2R't - I^2dR't - T\left(\frac{\partial E}{\partial T}\right)_n It\right]$$

Half the algebraic differences of these two equations is

$$J\left(\frac{\Pi' + \Pi''}{2}\right) = T\left(\frac{\partial E}{\partial T}\right)_p It + T\left(\frac{\partial E}{\partial T}\right)_n It,$$

and this is the quantity sought. It will be observed that the quantities $I^2R't$ and $I^2R''t$ have the same algebraic sign in both equations. This is because the resistance on the zinc side remains below the initial value and on the copper side above the initial value by reason of the change in concentration, and both reach their initial value again only when the reverse current has traversed the cell for as long a time as the direct current. The observations are then complete. The difference in heat development on the two sides is less than the normal at the close of the direct current flow and more than the normal during the flow of the reverse current. The half sum of the two is the mean or normal value.

In the later experiments the thermometers were discarded and two thermal couples consisting of thin iron and "constantan" wires, were substituted for them. The junctions were thickly covered with shellac and were inclosed in thin glass tubes with enough mercury to cover the soldered joints to aid in the conductivity of heat. One junction was placed in the zinc sulphate, the other in the copper sulphate. The plates of the cell were attached to the glass tubes containing the thermal junctions, and the tubes in

turn were held by rubber bands to two long, thin rods of wood held firmly at their upper ends. The stirring of the liquids was thus easily accomplished by bending the wooden rods.

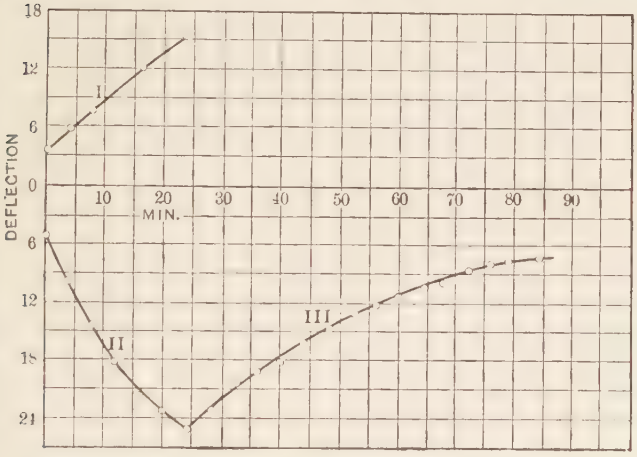


Fig. 21

The galvanometer connected in series with the thermal couples was astatic and sufficiently sensitive, but its period was about 20 seconds. The reading telescope was placed at a distance of 2.8 m., and the reduced deflection per degree difference of temperature was 138.3 mm. The zero position was unfortunately a drifting one, so that the cross wire of the telescope had to be set on it before every reading. The liquids were

DIRECT CURRENT

Time in min.	Reading, Deflection and Cooling Correction					
	0.02		0.03		0.04	
0	3.6		4.0		1.0	
		....		0.2		..
5	4.6		8.5		3.7	
		....		1.1		....
10	6.0		11.0		5.0	
		....		1.4		0.2
15	6.4		12.5		7.5	
		0.2		1.4		0.6
20	7.3		14.0		8.6	
		0.4		1.6		0.9
25	7.7		15.0		10.0	
		0.5		1.7		1.1
30	8.0		16.2		11.1	
		0.6		1.8		....
35	8.3		16.5		....	
		0.7		1.9		....
40	8.5		16.8		.. .	
		0.8	....			....
45	9.0		....		. .	
		0.9	....			....
50	9.1		....		....	
		1.0	....			...
55	9.5		....		....	
		1.1	....			....
60	10.0		....		....	
		6.4		12.8		10.1
Corrected deflections		12.6		23.9		12.9

REVERSE CURRENT

Time in min.	Reading, Deflection and Cooling Corrections					
	0.02		0.03		0.04	
0	2.8		−0.2		3.3	
5	6.9	0.7	3.0		8.7	0.2
10	10.0	1.2	5.0	0.2	13.2	1.2
15	12.0	1.3	7.7	0.3	16.9	1.6
20	13.3	1.5	9.2	1.1	20.0	2.1
25	14.4	1.6	10.9	1.4	22.8	2.4
30	15.5	1.8	12.0	1.5	24.8	2.8
35	16.8	1.9	13.7	1.6		
40	17.2	2.0	14.6			
45	17.5	2.0				
50	17.8	2.1				
55	18.5	2.1				
60	18.6					
		15.8		14.8		21.5
Corrected deflections		34.0		21.4		31.8
Half sums		23.30		22.65		22.35

DIRECT CURRENT

Time in min.	Readings, Deflections and Cooling Corrections					
	0.05		0.05		0.06	
0	2.0		3.6		0.0	
		.....		.....		.....
4	5.0		5.8		4.1	
		0.2		0.2		.....
8	7.0		7.9		6.8	
		0.4		0.8		0.7
12	7.0		9.6		10.0	
		0.5		1.0		0.9
16	8.9		12.0		11.3	
		0.7		1.1		1.1
20	9.0		13.8		12.7	
		1.0		1.2		.....
24	10.8		15.4		....	
		8.8		11.8		12.7
Corrected deflections		11.6		16.1		15.4

stirred for fifteen seconds before readings were taken. Five seconds intervened between the stirring and the observation.

With this arrangement the object in view was to determine, first, whether the temperature difference per second is proportional to the current, as equation (6) requires; second, how nearly the observed value of any established temperature difference agrees with the calculated value.

REVERSE CURRENT

Time in min.	Readings, Deflections and Cooling Corrections					
	0.05		0.05		0.06	
0	−4.0		4.8		1.0	
		.....		0.3		....
4	2.8		9.8		8.7	
		.....		1.1		1.0
8	8.0		14.1		13.2	
		0.9		1.4		1.4
12	12.5		18.2		18.5	
		1.3		1.8		1.8
16	16.6		21.5		22.8	
		1.6		2.1		2.3
20	19.4		23.3		26.0	
		2.0		2.3		.....
24	23.0		26.0		....	
		27.0		21.2		25.0
..	.		. . .		....	
		32.8		30.2		31.5
Half sums		22.20		23.15		23.45
Mean of all				22.85		

Figure 21 shows the results of one series with a current of 0.05 ampere. Curve I belongs to the observations with a direct current, curve II to those with the current reversed, and III is the "cooling curve." Many observations were taken for curve III, all of them agreeing well with this series.

The third, fifth and seventh columns of corrections were taken from the "cooling curve," which was drawn on a large scale on finely divided square paper. They correspond to the several intervals, five minutes or four minutes, and to the deflections. The last numbers in these same columns are the differences between the first and last deflections. To these are added the whole column of successive separate corrections for the final corrected reading.

The tables contain all the essential data for the several currents used.

A deflection of 22.85 scale parts corresponds to a difference of temperature of 0.165°. If the phenomenon here measured is proportional to the current, then since the quantities of electricity transmitted with the several currents were all equal, the resulting corrected deflections should be equal.

Current	Period in min.	Half sum	Variation from Mean
0.02	60	23.30	+0.45
0.03	40	22.65	−0.20
0.04	30	22.35	−0.50
0.05	24	22.20	−0.65
0.05	24	23.15	+0.30
0.06	20	23.45	+0.60

It is obvious that the heat generated on one side of the cell and that absorbed on the other are both proportional to the current in the case of the Daniell cell.

To calculate the difference of temperature between the two halves of the cell, it must be remembered that equation (6) expresses only the heat required to keep the temperature of the whole cell constant during the passage of a quantity of electricity. To calculate the quantity corresponding to the observed mean of 22.85 or 0.165°, we must find the calories generated on one side of the cell and absorbed on the other and divide their sum by the thermal capacity of half the cell. For this purpose we have the following data:

$$1/J = 0.24 \qquad T = 292$$

$$\left(\frac{\partial E}{\partial T}\right)_n = 0.00079 \qquad \left(\frac{\partial E}{\partial T}\right)_p = 0.00074$$

The first is for a range of temperature of 8.8° near 23°; the second is for a range of temperature of 5.6° near 19°.

dq or $Q = 72$ coulombs.

Hence $H = 0.24 \times 0.00079 \times 292 \times 72 = 3.99$ (zinc side)

and $H = 0.24 \times 0.00074 \times 292 \times 72 = 3.73$ (copper side).

The specific heat per unit volume of the solution is 0.99. The mean of two determinations of the thermal capacity of the unfilled cell was 16.5. Hence the thermal capacity of one-half the cell is

$$40 \times 0.99 + 8.25 = 47.85.$$

The temperature difference produced by the passage of 72 coulombs should then be

$$(3.99 + 3.73) \div 47.85 = 0.161°.$$

The mean observed value is 0.165°.

The difference between the observed and the computed value is only $2\frac{1}{2}$ per cent. One could scarcely expect better agreement in the case of measurements fraught with so many difficulties.

If H denotes the change in the internal energy of a Voltaic cell during the transport of F coulombs through an electrolyte by one gram equivalent of a cation, whose valence is n, then $H = nFE$ and the value of E corresponding to this change of internal energy is H/nF. To express the emf of the cell there must be added to this the thermo or Peltier emf,

$$T\left(\frac{dE}{dT}\right) = T\left(\frac{\partial E}{\partial T}\right)_p + T\left(\frac{\partial E}{\partial T}\right)_n.$$

This gives finally the famous Helmholtz equation

$$E = \frac{H}{nF} + T\frac{dE}{dT}.$$

CHAPTER VI

ELECTROMOTIVE FORCE OF CONCENTRATION CELLS

26. The Nernst and the Helmholtz Formula for the EMF of Concentration Cells. — It is interesting to examine the conditions under which the temperature coefficient of the emf of a concentration cell is so nearly equal to the temperature coefficient of gas pressure; that is, why "the increase of the potential with increase of temperature is identical with the increase of pressure for a perfect gas." [1]

An instructive series of relations, expressing the several quantities as a function of the temperature, will serve as a fitting point of departure for this discussion. These relations are the following:

$P = P_0(1 + at)$, for the pressure of a gas at constant volume.

$p = p_0(1 + at)$, for osmotic pressure.

$R = R_0(1 + at)$, for the resistance of pure metals.

[1] Publication No. 56, 1906, Carnegie Institution of Washington.

$E = E_0(1 + at)$, for electrolytic thermo-electromotive force of infinitely dilute solutions.

The coefficient a has the same value in all four equations. It is $1/273$ or 0.00366 very approximately, at least for the pressure of an ideal gas, most nearly represented by hydrogen; for the resistance of pure platinum; and for the emf of any concentration cell with solutions indefinitely dilute. It is an interesting inquiry as to what is the common relationship indicated by the common constant a equal to $1/273$.

The differential coefficient of pressure with respect to temperature from the first equation is $dP/dT = P_0 a$; from which we have $a = 1/P_0 \cdot dP/dT$ as the most general expression for the temperature coefficient, with corresponding expressions for the other three relations.

If now P, for example, is zero at the absolute zero of temperature, then $0 = P_0(1 - 273a)$ and $a = 1/273 = 1/T_0$. Substitute this value of a in the equation above, and $dP/dT = P_0/T_0$. Whence $P_0 = T_0 \cdot dP/dT$. Similarly in general, $P = T \cdot dP/dT$; that is, *the pressure is proportional to the temperature on the absolute scale.* Corresponding expressions may be derived for the other quantities. If R is zero at the absolute

zero of temperature, then $R = T \cdot dR/dT$ and $a = 1/T_0$. So also if E is zero at the zero of the absolute scale, then $E = T \cdot dE/dT$ and a for that relation is also $1/T_0$.

If in each of the four relations the quantity represented becomes zero at the zero of the absolute scale, on the assumption that the law holds down to that point, then the temperature coefficient a is $1/T_0$. Each equation may then serve to define and evaluate the absolute zero; and if this zero denotes anything real, such as the zero of heat energy, then the T_0's for the several equations may be expected to coincide. As a matter of fact, the coefficient a is practically the same in all four equations, and the corresponding absolute zeros are therefore approximately identical.

In the case of pure platinum Dewar and Fleming have extended experimentally the straight line graph connecting its resistance and temperature so far down the scale toward absolute zero that they are able to say that it runs nearly through -273° C. The common constant a means that gas pressure (volume constant), osmotic pressure, electrical resistance, and electromotive force (under definite conditions) are all proportional to the absolute temperature.

If R has a positive value at the absolute zero, as it has in the case of alloys, then

$$R = R_{-273} + T\frac{dR}{dT}.$$

R_0 is then greater than $T_0 \cdot dR/dT$ and a is less than $1/T_0$. So also E at the absolute zero may have either a positive or a negative value, and then

$$E = E_{-273} + T\frac{dE}{dT}.$$

27. The Helmholtz Equation. — The famous Helmholtz equation for the electromotive force of a voltaic cell is

$$E = \frac{H}{nF} + T\frac{dE}{dT},$$

corresponding with the last equation above. In the Helmholtz equation H is the heat of reaction or of dilution, expressed in joules; n is the valence of the cation; and F is the number of coulombs transported by a gram-equivalent of the cation.

The term $T \cdot dE/dT$, proportional to the absolute temperature, is purely thermoelectric. It is now fully established and agreed that the coefficient dE/dT is the algebraic sum of the electromotive forces per degree arising at the

several thermal junctions in the cell. If this coefficient is positive, then the cell converts some of the heat of the cell and its surroundings into the energy of an electric current; if it is negative, the electrical energy given out is less than the heat of reaction and dilution, and the cell heats. In the former case heat is absorbed

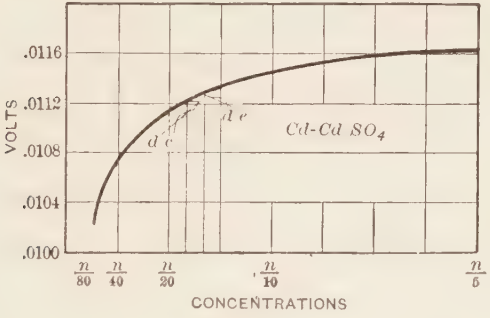


Fig. 22

and utilized; in the latter it is generated and wasted.

The second term of the Helmholtz equation denotes then thermoelectromotive force, and so does any other form of expression for electromotive force which is proportional to absolute temperature.

28. The Nernst Equation from Thermo-electromotive Force. — The curve in the accompanying figure exhibits the relation between the

concentration of the electrolyte ($CdSO_4 + H_2O$) and the electromotive force per degree C. The electrodes were the same cadmium amalgam in every case, the only variation being the concentration of the electrolyte.[1] From this curve one may write the equation connecting electromotive force and concentration as follows:

$$dE = bT\frac{dc}{c}.$$

In this equation b is a proportionality factor and c is the concentration. Since this is thermo-emf, there appears to be abundant reason for assuming that the increment of the emf is proportional to the temperature T on the absolute scale. Also it is proportional to the increment of the concentration dc, but the curve shows that it decreases in value as the concentration increases. Hence the equation for dE. Integrating

$$E = bTlnc + \text{a constant}.$$

But when T is zero, E is zero, and therefore the integration constant is zero. Therefore $E = bTlnc$ (ln is the natural logarithm). This expression is the potential difference arising at a single electrode. For a cell with different con-

[1] Trans. Amer. Electrochemical Soc., Vol. II, p. 126; also Phys. Rev., Vol. XXV, p. 357.

centrations of the same electrolyte at the two electrodes, the emf is the difference between the two electrode potentials, or

$$E = bTlnc_2 - bTlnc_1 = bTln\frac{c_2}{c_1}.$$

It will be recognized that this equation agrees in form with that of Nernst, or at least of his pupils, for the emf of a concentration cell:

$$E = \frac{R}{nF}Tln\frac{c_2}{c_1}.$$

The Nernst equation, or its equivalent above, is only a variation of the second term of the Helmholtz equation; for the differential coefficient of E with respect to T from the first equation above is

$$\frac{dE}{dT} = bln\frac{c_2}{c_1}, \text{ and } b = \frac{dE}{dT} \div ln\frac{c_2}{c_1}.$$

Substitute this value of b in the equation for E, and we have

$$E = T\frac{dE}{dT}.$$

The Nernst equation is therefore only another form of expression for that part of the emf of a concentration cell arising from electrolytic thermo-electromotive force; and it gives the correct value for the emf of such a cell only for in-

finite dilution, or when the heat of dilution is negligible. When there is no heat of dilution, the first term of the Helmholtz equation is zero and only the term expressive of thermo-electromotive force remains.

29. The Research of Richards and Forbes. — These conclusions find ample justification in two directions:

1. In the research of Richards and Forbes, published by the Carnegie Institution of Washington, and entitled "Energy Changes Involved in the Dilution of Zinc and Cadmium Amalgams." [1]

2. In the results of a research in my laboratory under the skilled hand of Dr. F. J. Mellencamp. In this research the observed and computed electromotive forces are compared for concentration cells with solutions of various degrees of dilution.

The research of Professor T. W. Richards and Mr. Forbes is a thorough, careful and admirable piece of work. They measured the electromotive force of concentration cells in which the difference of concentration was in the amalgams composing the electrodes, an electrolyte of one concentration only being employed. The heat of

[1] Publication No. 56, 1906

dilution of the amalgams was measured directly by a special calorimeter. The dilution of a 0.9 per cent zinc amalgam with an equal weight of mercury *absorbed* heat at the rate of 52 joules per gram-molecule of zinc; that is, the dilution of zinc amalgam has a cooling effect. The heat of dilution of a 3 per cent cadmium amalgam was so small as to defy direct measurement.

The authors say on page 60: "One of the striking facts in relation to cadmium amalgam is the fact that its heat of dilution is so small as to be negligible. Therefore, the equation of Helmholtz reduces practically to the form

$$E = T\frac{dE}{dT},$$

making the thermodynamics of the problem as simple as possible." [1]

Now under these conditions the temperature coefficient a reduces to $1/T_0$. For since

$$E_0 = T_0\frac{dE}{dT},$$

the coefficient

$$\frac{1}{E_0}\frac{dE}{dT} = \frac{dE}{dT} \div T_0\frac{dE}{dT} = \frac{1}{T_0}.$$

[1] I have changed the nomenclature to agree with that commonly employed by physicists.

The agreement of this coefficient with that of gas pressure signifies merely that the electromotive force is very approximately proportional to T, the absolute temperature, for then a always equals 1/273 or 0.00366.

The accuracy of the work of Richards and Forbes is attested by the fact that the measured temperature coefficient for the cadmium amalgams is very close to 0.00366. On this point I quote the following:

"It becomes now a matter of great interest to compare this change of potential with the requirements of the gas law, by comparing the temperature coefficient with the temperature-pressure coefficient of a perfect gas over the same range of temperature.

"The following table gives the temperature coefficients referred to the observed potentials at zero:

2–4, from 30° to 15.2°.

$$\frac{1}{E_0}\frac{\Delta E}{\Delta T} = \frac{0.001659}{14.8 \times 0.030826} = 0.00364$$

2–4, from 15.2° to 0.0°.

$$\frac{1}{E_0}\frac{\Delta E}{\Delta T} = \frac{0.001719}{15.2 \times 0.030826} = 0.00367$$

1–4, from 30° to 15.2°.

$$\frac{1}{E_0}\frac{\Delta E}{\Delta T} = \frac{0.002578 \times 288.2}{14.8 \times 0.050332 \times 273} = 0.003665$$

1–3, from 30° to 15.2°.

$$\frac{1}{E_0}\frac{\Delta E}{\Delta T} = \frac{0.00177 \times 288.2}{14.8 \times 0.03413 \times 273} = 0.00366$$

Average 0.003656

"The agreement is surprisingly good; within the limit of accuracy of the measurement the increase of the potential with increase of temperature is identical with the increase of pressure of a perfect gas."

Professor Richards regards this agreement of the electromotive force coefficient with the pressure coefficient, both with respect to temperature, as a proof that the gas law, $pv = RT$, applies to a concentration cell. On the contrary, it appears from this discussion that this agreement of coefficients means only that the electromotive force of a concentration cell, with negligible heat of dilution, is proportional to the absolute temperature.

It is particularly unfortunate that these investigators did not determine the temperature coefficient for pairs of zinc amalgams, for it is certain that they would have found a value greater than 0.00366, except in the case of very

dilute amalgams. They did *calculate* one temperature coefficient for zinc amalgams and found it to be 0.00379.

The identity of the temperature coefficient with $1/273$ is not a satisfactory proof even that the heat of dilution is negligible, for the electromotive force due to heat of dilution affects only the value of E_0 in the expression for the temperature coefficient, $1/E_0 \cdot dE/dT$, and a moderately small change in the denominator of a small fraction produces a nearly negligible change in the value of the fraction itself.

A better criterion to apply as a test of the presence or absence of heat of dilution is to compare the measured values of electromotive force with those derived from the expression $T \cdot dE/dT$, or its equivalent in the form of the Nernst equation.

When the heat of dilution is negative, the first term of the Helmholtz equation is also negative, and the emf of the cell is less than $T \cdot dE/dT$. When the heat of dilution is positive, the first term of the Helmholtz equation is positive, and the emf of the cell is greater than $T \cdot dE/dT$.

It will be observed that the electromotive forces for the zinc amalgams are smaller than

the values derived from the Nernst formula. Moreover, for very dilute amalgams the curve approaches indefinitely near the theoretical value of the Nernst formula. The zinc amalgams show much larger deviations from the computed values than do the cadmium amalgams. Since the Nernst equation is only the equivalent of the second term of the Helmholtz equation, it is useless to attempt to correct the Nernst formula so as to make it cover the case of concentration cells in which there is heat of dilution to affect the value of the emf. It applies only to cells with infinite dilutions. The second term only of the Helmholtz equation is proportional to the absolute temperature. The first term, while not necessarily independent of temperature, is not proportional to it and cannot therefore be included in the Nernst equation or in any modification of it, unless another term is added.

30. The Research of Mellencamp.[1] — The preceding conclusions, involving a comparison of the Helmholtz and Nernst equations, are completely justified by the measurements on a series of concentration cells made with solutions of electrolytes whose heats of dilution are known. In most of these cases the concentrations are

[1] Physical Rev., Vol. XXIX, 1909, p. 329.

such that the heats of dilution are relatively large, and the first term of the Helmholtz equation cannot be neglected. No better justification of the Helmholtz equation than these results has ever been presented.

Whenever the heat of dilution of the solutions in the two legs of a concentration cell is appreciable, it is available as energy to produce electromotive force, represented by the first term of the Helmholtz equation. The electrode in the more dilute solution is the anode. Let us suppose the quantities of the two solutions so large that the entrance of a gram-equivalent of the metal at the anode and the removal of an equal quantity from the solution about the cathode do not change the concentrations of the solutions. Then when a gram-equivalent of the metal at the anode becomes a salt, it is diluted down to the same concentration as that of the solution surrounding the anode; at the same time a gram-equivalent of the same metal is removed from the more concentrated solution surrounding the cathode. This latter operation absorbs less energy than is derived from the former, if the heat of dilution is positive; and this surplus energy is available to produce electromotive force.

To illustrate: One gram-molecule of $ZnSO_4 \cdot 20H_2O$ diluted to $ZnSO_4 \cdot 50H_2O$ generates 318 calories of heat (Thomsen). Also, $ZnSO_4 \cdot 20H_2O$ diluted to $ZnSO_4 \cdot 400H_2O$ generates 400 calories. Hence, $ZnSO_4 \cdot 50H_2O - ZnSO_4 \cdot 400H_2O$ is equivalent to the difference between 400 and 318, or 82 calories. If a cell is set up with these two solutions, the emf corresponding to this difference in the heats of dilution is

$$\frac{82 \times 4.189}{2 \times 96{,}500} = 0.00178 \text{ volt.}$$

The coefficient dE/dT of a cell set up with electrodes of liquid zinc amalgam in the above solutions is positive and equal to 0.0000528, as a mean of several determinations. Hence, for 25° C. the term $T \cdot dE/dT$ is $298 \times 0.0000528 = 0.01573$. Then

$$E = 0.00178 + 0.01573 = 0.0175 \text{ volt.}$$

The observed emf at 25° was 0.0171.

By applying the additive principle, three checks are obtained on the direct measurement of cell 1. The sum of 2 and 6 should equal 1; the sum of 3 and 4 should also equal 1; 4, 5 and 6 should equal 1. We thus obtain four independent values for the cell made up of $Zn \cdot Hg - ZnSO_4 \cdot 50H_2O - ZnSO_4 \cdot 400H_2O - Zn \cdot Hg$; and 10 gives

TABLE I

Solutions	Cells	$\frac{dE}{dT}$	$T\frac{dE}{dT}$ at 25°	E_h	Comp. emf	Obs. emf
$ZnSO_4 \cdot 50H_2O$	1*a*	0.0000528	0.01573	0.00178	0.01751	0.01713
	1*b*	0.0000524	0.01561	.....	0.01739	0.01710
$ZnSO_4 \cdot 400H_2O$	1*c*	0.0000510	0.01520	.....	0.01698	0.01701
	1*d*	0.0000510	0.01520	.....	0.01698	0.01711
	1	0.0000518	0.01544	0.00178	0.01722	0.01709
$ZnSO_4 \cdot 50H_2O$	2*a*	0.0000352	0.01029	0.00145	0.01193	0.01162
	2*b*	0.0000344	0.01045	.....	0.01170	0.01159
$ZnSO_4 \cdot 200H_2O$	2*c*	0.0000340	0.01013	.....	0.01158	0.01139
	2	0.0000345	0.01029	0.00145	0.01174	0.01153
$ZnSO_4 \cdot 100H_2O$	3*a*	0.0000340	0.01013	0.00072	0.01085	0.01090
	3*b*	0.0000344	0.01025	.....	0.01097	0.01090
$ZnSO_4 \cdot 400H_2O$	3*c*	0.0000344	0.01025	.....	0.01097	0.01081
	3	0.0000343	0.01021	0.00072	0.01093	0.01087
$ZnSO_4 \cdot 50H_2O$	4*a*	0.0000174	0.00518	0.00106	0.00624	0.00628
$ZnSO_4 \cdot 100H_2O$	4*b*	0.0000160	0.00477	.....	0.00583	0.00607
	4	0.0000167	0.00498	0.00106	0.00604	0.00618
$ZnSO_4 \cdot 100H_2O$	5*a*	0.0000172	0.00512	0.00039	0.00551	0.00541
$ZnSO_4 \cdot 200H_2O$	5*b*	0.0000180	0.00536	.....	0.00575	0.00552
	5	0.0000176	0.00524	0.00039	0.00563	0.00547
$ZnSO_4 \cdot 200H_2O$	6*a*	0.0000164	0.00489	0.00033	0.00522	0.00543
$ZnSO_4 \cdot 400H_2O$	6*b*	0.0000180	0.00536	.....	0.00569	0.00556
	6	0.0000172	0.00513	0.00033	0.00546	0.00550
2 + 6	7	0.0000517	0.01542	0.00178	0.01720	0.01703
4 + 3	8	0.0000510	0.01519	0.00178	0.01697	0.01705
4 + 5 + 6	9	0.0000515	0.01535	0.00178	0.01713	0.01715
Mean of 1, 7, 8, 9	10	0.0000515	0.01535	0.00178	0.01713	0.01708

the mean of these four. The agreement will be found to be very satisfactory. The difference between the computed and observed values of the mean emfs is about one-fourth of one per cent. Of the sixteen cells recorded in the table, the heat of dilution accounts for from five to eighteen per cent of the whole emf of the cell. The Helmholtz equation applies rigorously, the deviation between the computed and the observed values being less than the probable experimental errors, especially as the determination of the heats of dilution was made many years ago, and needs to be repeated.

The amalgams used in these measurements contained a little less than one per cent of zinc.

The heat of dilution for the solutions in the zinc sulphate cells is relatively small, and it accounts for only a small per cent of the total emf of the cell, the remainder being due to the term $T \cdot dE/dT$ expressing the heat absorbed from the surroundings by means of the Peltier emf. In the case of cadmium sulphate the heat of dilution is relatively large, and it accounts for a large part of the emf of cadmium concentration cells. Concentration cells of cadmium sulphate and cadmium amalgam electrodes are very constant so long as the cadmium amalgam is not

TABLE II

Solutions	Cells	$\frac{dE}{dT}$	$T\frac{dE}{dT}$ at 25°	E_h	Comp. emf	Obs. emf
$CdSO_4 \cdot 30.6H_2O$	1*a*	0.0000235	0.00700	0.01565	0.02265	0.02205
$CdSO_4 \cdot 400H_2O$	1*b*	0.0000244	0.00727	.....	0.02292	0.02213
	1*c*	0.0000210	0.00626	.....	0.02191	0.02213
	1	0.0000230	0.00684	0.01565	0.02249	0.02210
$CdSO_4 \cdot 30.6H_2O$	2*a*	0.0000080	0.00238	0.00960	0.01199	0.01176
$CdSO_4 \cdot 100H_2O$	2*b*	0.0000078	0.00231	.....	0.01191	0.01170
	2	0.0000079	0.00235	0.00960	0.01195	0.01173
$CdSO_4 \cdot 100H_2O$	3*a*	0.0000155	0.00462	0.00604	0.01066	0.01025
$CdSO_4 \cdot 400H_2O$	3*b*	0.0000156	0.00465	.....	0.01069	0.01038
	3*c*	0.0000160	0.00477	.....	0.01081	0.01052
	3	0.0000157	0.00468	0.00604	0.01072	0.01038
$CdSO_4 \cdot 50H_2O$	4*a*	0.0000192	0.00572	0.01082	0.01654	0.01638
$CdSO_4 \cdot 400H_2O$	4*b*	0.0000200	0.00596	.....	0.01678	0.01637
	4*c*	0.0000185	0.00551	.....	0.01633	0.01615
	4	0.0000192	0.00573	0.01082	0.01655	0.01629
$CdSO_4 \cdot 50H_2O$ $CdSO_4 \cdot 200H_2O$	5	0.0000090	0.00268	0.00747	0.01115	0.01107
$CdSO_4 \cdot 200H_2O$ $CdSO_4 \cdot 400H_2O$	6	0.0000095	0.00283	0.00234	0.00517	0.00496
2 + 3	7	0.0000236	0.00703	0.01565	0.02268	0.02211
5 + 6	8	0.0000185	0.00551	0.01082	0.01633	0.01603

very dilute. One cell was examined for a period of eighteen days, and after reaching equilibrium, the maximum change in emf was only 0.00003 volt. Six per cent amalgams were chosen because this is liquid except at low temperatures. The measurements were all made at 25° and 40°. At lower temperatures the solid phase appears.

In this table cells 2 and 3 should equal 1, and 5 and 6 should equal 4. The agreement is satisfactory, but it is not quite so close as in the case of the zinc sulphate cells. The heat of dilution accounts for from fifty to eighty per cent of the emf of these cells.

In the case of zinc amalgam and solutions of the sulphate of zinc of different concentration both terms of the Helmholtz equation are positive; that is, the heat of dilution is positive; also the electrolytic thermo-emf is positive. But with zinc amalgam and solutions of zinc chloride the temperature coefficient or the electrolytic thermo-emf is negative. That is, the second term of the Helmholtz equation is negative. Further, in the case of lead amalgam and solutions of lead nitrate the heat of dilution is negative, and the first term of the Helmholtz equation is negative. The data for the two are contained in Table III.

TABLE III

Solutions	Cells	$\frac{dE}{dT}$	$T\frac{dE}{dT}$ at 25°	E_h	Comp. emf	Obs. emf
$ZnCl_2 \cdot 18 \cdot 8H_2O$	*a*	− 0.000097	− 0.02891	0.09832	0.06941	0.06722
	b	− 0.000098	− 0.02920	0.09832	0.06912	0.06723
$ZnCl_2 \cdot 180H_2O$	*c*	− 0.000097	− 0.02891	0.09832	0.06941	0.06712
		− 0.000097	− 0.02901	0.09832	0.06931	0.06719
$Pb(NO_3)_2 \cdot 100H_2O$	*a*	0.000146	0.04351	− 0.02756	0.01595	0.01620
	b	0.000145	0.04321	− 0.02756	0.01565	0.01632
$Pb(NO_3)_2 \cdot 400H_2O$	*c*	0.000141	0.04202	− 0.02756	0.01446	0.01636
		0.000144	0.04219	− 0.02756	0.01535	0.01629

The mean observed emf for the zinc chloride cells differs from the mean computed value by three per cent; in the case of the lead nitrate the difference is six per cent. The zinc chloride suffers hydrolysis and the lead amalgam oxidizes. Closer agreement could therefore hardly be expected.

CHAPTER VII

THERMODYNAMICS OF CONCENTRATION CELLS

31. Thermodynamics of an Isothermal Process. — The most general expression of the laws of thermodynamics for an isothermal process, of which the well-known equation of Helmholtz for the electromotive force of voltaic cells is a particular example, may be written in the form

$$A = H + T\frac{dA}{dT}.$$

H denotes the change in the internal energy of the system and A the maximum work or the change of free energy for a reversible physical or chemical process conducted isothermally.

If A for 1 gram-equivalent of an ion is expressed in terms of electrical work as nFE (n the valence of the cation, F the number of coulombs transported through an electrolyte by a gram-equivalent, and E the emf), the equation becomes that of Helmholtz, namely,

$$nFE = H + TnF\frac{dE}{dT}, \text{ or } E = \frac{H}{nF} + T\frac{dE}{dT}.$$

A number of distinct cases occur in the application of the general equation.

First. $dA/dT = 0$ at all temperatures. This case is an expression of the so-called Thomson principle as applied to voltaic cells, which makes $dE/dT = 0$. In fact, the Daniell cell, set up with saturated copper sulphate and very dilute zinc sulphate (specific gravity 1.04)[1] as the electrolytes, and the Weston cell without cadmium sulphate crystals, have electromotive forces very nearly independent of temperature. They may therefore be classed under this head.

Another case in point is the purely physical transformation of the potential energy of gravity into the energy of electric transfer. The Des Coudres' cell,[2] consisting of two mercury columns of different height, joined by a solution of mercurous nitrate, the longer column being retained in position by a porous diaphragm, is another illustration of case one. The measurement of the emf in this arrangement is not very satisfactory, but the results are of the same order of magnitude as the calculated values. A single example will suffice.

The difference between the measured heights

[1] Helmholtz: Sitzungsber. Berl. Akad., pp. 22–39, 1882.
[2] Wied. Ann., 46, p. 292, 1892.

of the columns was 141.1 cm. Then, when one gram-equivalent (200 g.) of mercurous mercury is transferred electrolytically from the one elevation to the other, the decrease in potential energy is $141.1 \times 200 \times 980 = 27{,}655{,}600$ ergs $= 2.76556$ joules. The corresponding emf is $\frac{2.76556}{96530}$ $= 0.0000286$ volt; the measured value was 0.000030.

Second. H has a constant value. The general equation above gives $\frac{dA}{A - H} = \frac{dT}{T}$. By integration $\ln (A - H) = \ln T + \ln a = \ln aT$. Whence $A - H = aT$. Since a is the constant of integration, $A - H$ is proportional to the absolute temperature T and $dA/dT = a$. It appears, therefore, that when dA/dT or dE/dT is a constant, H is either zero or has a constant value. Illustrations will follow later.

Third. $A = 0$, and $H = -T.\, dA/dT$. This condition can obtain only at some definite point of temperature where A passes through a zero value. Examples are several cases of transition, such as $ZnSO_4 \cdot 7\, H_2O$ into $ZnSO_4 \cdot 6\, H_2O$ at 39°, and white tin into gray tin at 20°. At the transition temperature the two phases are in equi-

librium, like water and ice at 0°, and there is no free energy. But at the transition point dA/dT may be large, and $H = -T.dA/dT$.

Fourth. As a fourth case we may include Nernst's recent modification of the general equation. Nernst[1] assumes the following empirical expressions for A and H in terms of the integral powers of the absolute temperature:

$$A = A_0 + a'T + b'T^2 + c'T^3 +$$
$$H = H_0 + aT + bT^2 + cT^3 +$$

From the general thermodynamic equation, when $T = 0$, $A_0 = H_0$; hence

$$\frac{A - H}{T} = \frac{dA}{dT} = (a' - a) + (b' - b)T + (c' - c)T^2 = a' + 2b'T + 3c'T^2.$$

Whence $a' = a' - a$, or $a = 0$; $2b' = b' - b$, or $b' = -b$; $3c' = c' - c$, or $c' = -\frac{1}{2}c$. Finally, then,

$$A = A_0 + a'T - bT^2 - \tfrac{1}{2}cT^3 -$$
$$H = H_0 + bT^2 + cT^3 +$$

Since the same constants now appear in both equations, the a' may be replaced by a.

When the constants b and c are zero, the expression for A reduces to the simpler one containing only the first power of T, $A - H = aT$,

[1] Thermodynamics and Chemistry, Sitzungsber. Berl. Akad., 190

and $dA/dT = a$, a constant as in case two, or the relation between A and T is a linear one.

Nernst assumes without sufficient justification that both $\frac{dA}{dT}$ and $\frac{dH}{dT}$ are zero when T is zero. The equations above show that $\frac{dA}{dT} = a$ when $T = 0$; hence the term aT in the expansion for A is not zero as Nernst has it. If it were zero, the expression for A would exclude the case of concentration cells, in which A is proportional to the absolute temperature (for very dilute solutions), or is equal to a constant H plus a term proportional to the first power of the absolute temperature.

The same conclusion may be reached by a different demonstration, assuming only the one expansion,

$$H = H_0 + aT + bT^2 + cT^3 +$$

The general equation $A = H + T\frac{dA}{dT}$ gives

$$AdT - TdA = HdT, \text{ or } \frac{TdA - AdT}{T^2} = -\frac{H}{T^2}dT.$$

Integrating,

$$\frac{A}{T} = \frac{H_0}{T} + a' - a\ln T - bT - \tfrac{1}{2}cT^2,$$

$$\text{or } A = H_0 + a'T - aT\ln T - bT^2 - \tfrac{1}{2}cT^3.$$

Then $\frac{dA}{dT} = a' - a \ln T - a - 2bT - \frac{3}{2}cT^2.$

If now this expression for A is generally true, it must be true when dA/dT is a constant. But in case two it was shown that dA/dT is a constant when dH/dT is zero for $T = 0$, as in the last solution. Hence a in the expressions above for both A and H is zero, and the two reduce as before to

$$A = A_0 + a'T - bT^2 - \tfrac{1}{2}cT^3 -$$
$$H = H_0 + bT^2 + cT^3 +$$

The reader will note that these demonstrations show only that while the coefficient of T in the expansion for H is always zero, it is not necessarily zero in the expansion for A.

32. The Evidence of Experiment. — It would appear antecedently probable that a concentration cell such as Zn amal. conc. — $ZnSO_4$ solution — Zn amal. dil. (where the dilute amalgam at least must be of a lower concentration than that corresponding to a saturated or two-phase condition) should have constant heat of dilution for the two amalgams; or, in other words, H should be constant. This proves to be true, for the emf as a function of the temperature is linear.

For two amalgams with a concentration ratio by weight equal to two, the per cent of zinc in

the more concentrated amalgam being approximately 1.2, the equation representing the emf was found to be

$$E = -0.001455 + 0.00003084\ T.$$

For the centigrade scale this is equivalent to

$$E_t = 0.006964(1 + 0.00443\ t).$$

The constant 0.00443 is the temperature coefficient $\frac{1}{E_0}\frac{dE}{dT}$. It is much larger than the temperature coefficient of a perfect gas.

In the following table are the observed values of the emf compared with those computed by the first equation:

Temp.	Obs. emf	Comp. emf	Per cent difference
11.1°	0.007300	0.007307	+0.10
15.4°	7444	7439	− .07
19.8°	7574	7575	+ .01
24.6°	7720	7723	+ .04
29.4°	7870	7871	+ .01
32.8°	7983	7976	− .09
36.6°	8086	8094	+ .10
42.0°	8262	8259	− .04
47.0°	8417	8414	− .04

The greatest difference between the observed and the computed value is 0.008 millivolt. The experimental cell was placed in a large water bath with double walls, and a stirrer driven by

an electric motor was used to insure equal temperatures of the two legs of the cell. The emf was measured by a Wolff's potentiometer and a Weston normal cell.

The cell was then taken apart, the amalgams washed, and the cell was again assembled with a concentrated solution of $ZnCl_2$ as the electrolyte. The observations are best represented by the same linear equation as the one applying to the $ZnSO_4$. Both the heat of dilution of the amalgams and the temperature coefficient, therefore, remain unchanged when the anion Cl^2 replaces the anion SO_4. The observed and computed values are compared in the table.

Temp.	Obs. emf	Comp. emf	Per cent difference
10.1°	0.007275	0.007276	+0.01
14.9°	7424	7424	.00
19.6°	7567	7569	+ .03
25.3°	7733	7744	+ .14
32.1°	7943	7954	+ .14
37.3°	8106	8114	+ .10
41.8°	8256	8253	− .04
47.9°	8460	8441	− .22
49.3°	8486	8485	− .01

In the diagram Fig. 23 the circles denote the observations for $ZNSO_4$ and the crosses those for $ZnCl_2$.

Bouty found the emf for zinc amalgam in all salts of zinc the same.[1]

He calls attention to the fact that two copper electrodes plunged into sulphate of copper on one side and acetate of copper on the other gave an emf of about 0.037 volt with the copper in the acetate as the positive electrode. Further,

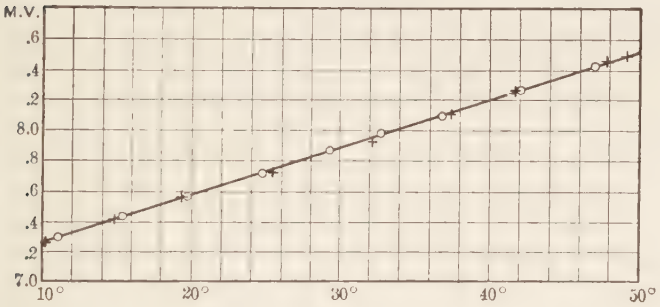


Fig. 23

this emf was not modified by elevation of the temperature of the couple since the thermo-emfs at the two metal-liquid junctions were equal and opposed.

The equality of the thermo-emfs between zinc amalgam and the sulphate and the chloride of zinc suggested that a cell made up of zinc amalgam in zinc sulphate on one side and zinc chloride on the other would show a zero temperature

[1] Jour. de Phys., 9, 1880, p. 236.

coefficient. The zinc amalgam contained about 1.2 per cent of zinc and the sulphate and the chloride solutions were both saturated. The cell had an emf of 0.0422 volt, the zinc amalgam in the sulphate solution being the positive electrode. The emf remained the same at 1.5° and 21.5°. Thus the temperature coefficient between these limits was zero, confirming the equality of the two opposed metal-liquid thermo-emfs on opposite sides of the cell.

33. The Constancy of dE/dT. — Since the equation representing the emf is linear, it follows that dE/dT is a constant. The constancy of dE/dT may be shown in another manner. From the Helmholtz equation and the constant of the last equation, $\frac{dE}{dT} = \frac{E + 0.001455}{T}$.

Then for

11.1°, $\frac{dE}{dT} = \frac{0.007300 + 0.001455}{284.1}$	=	0.00003082
15.4°		3085
19.8°		3083
24.6°		3083
29.4°		3083
32.8°		3086
36.6°		3082
42.0°		3085
47.0°		3085
Mean		0.00003084

Cady [1] measured the emf of a sodium amalgam cell with the amalgams in a solution of NaI in pyridin. He assumed the correctness of the formula in the Nernst form for the emf of the cell as $0.0002\ T \log \frac{c_1}{c_2}$, in which the ratio of the concentrations replaces that of the osmotic pressures of the sodium in the amalgams. From his data the following values have been calculated:

$$\text{For } 4^\circ,\ \frac{dE}{dT} = \frac{0.0648 - 0.03}{277} = 0.0001256$$

7°	1264
9°	1262
19°	1260
22°	1264
Mean	0.0001261

The constant 0.03 was the difference between the observed electromotive forces and those calculated from the Nernst formula. This constant is evidently too large. Calculating it by the Helmholtz equation for 7°, for example, it is 0.0265. Then, substituting this in place of 0.03 in the equation for dE/dT, the resulting value is 0.0001384. Again correcting the heat of dilution by this new approximate value of dE/dT,

[1] Jour. Phys. Chem., 2, 1898.

the emf due to the heat of dilution comes out 0.02665. The substitution of this value in place of 0.03 in the Helmholtz equation to determine dE/dT gives as the mean value 0.0001381. This is materially larger than Cady's value from the same data.

The equation for the emf is accordingly

$$E = 0.02665 + 0.0001381\ T.$$

The observed and computed values are the following:

Temp.	Obs. emf	Comp. emf	Per cent difference
4°	0.0648	0.06480	0.0
7°	654	6532	− .12
9°	656	6559	− .02
19°	668	6698	+ .25
22°	673	6729	− .02

The heat of dilution of the sodium amalgam with mercury, computed from the equation for E, is 612.9 calories per gram-molecule.

The following examples have been calculated from data given by Richards (Carnegie Institution of Washington, Publication No. 118):

Thallium, per cent of metal in the denser amalgam, 0.41.

For 0°, $\frac{dE}{dT} = \frac{0.031543 - 0.001813}{273} = 0.0001089$

$$15^\circ \qquad \frac{0.033166 - 0.001813}{283} = 0.0001089$$

$$30^\circ \qquad \frac{0.034810 - 0.001813}{303} = 0.0001089$$

Thallium, per cent of metal in denser amalgam, 0.111.

$$\text{For } 0^\circ, \frac{dE}{dT} = \frac{0.016360 - 0.000436}{273} = 0.00005833$$

$$15^\circ \qquad \frac{0.017238 - 0.000436}{288} = 0.00005833$$

$$30^\circ \qquad \frac{0.018110 - 0.000436}{303} = 0.00005833$$

The linear equations for these two cases are:

$$E = 0.001813 + 0.0001089\ T.$$
$$E = 0.000436 + 0.00005833\ T.$$

The heat of dilution and the temperature coefficient are constant in both cases; both therefore negative the hypothesis of Nernst that the coefficient of T in the expression for A (or E) is zero. The relation between the emf and the temperature in all these amalgams is a purely linear one. The range of temperatures must be restricted to limits within which there is no change of phase in the materials composing the cell.

34. The Second Term of the Helmholtz Equation. — The term $T \cdot dE/dT$, in cases where there is no change of phase in the materials, is a purely electrolytic thermo-electromotive force, which is very approximately linear. To illustrate this feature as applied to concentration cells, two amalgams were made by weighing out masses of mercury as one to two and depositing in them electrically the same quantity of zinc. The weight of zinc deposited was 0.6 and 1.2 per cent, respectively, of the weight of mercury. The concentration cell set up with these amalgams and a dense solution of zinc sulphate gave the following electromotive forces at the temperatures indicated:

Temp.	Obs. emf	Comp. emf
10.70°	0.007320	0.007319
14.13°	7420	7420
19.62°	7572	7581
24.20°	7713	7716
26.25°	7785	7776
31.60°	7940	7933
36.80°	8086	8086
39.00°	8146	8151

Equation: $E = -0.001022 + 0.0000294\ T$.

The corresponding heat of dilution of the two amalgams is -47 calories per gram molecule.

35. Case of a Negative Temperature Coefficient. — When the difference in concentration is in the electrolyte surrounding the electrodes, cases occur of positive heat of dilution and a negative temperature coefficient. An example is the following:

$$Zn \mid ZnCl_2 \cdot 21.9\ H_2O \mid ZnCl_2 \cdot 386\ H_2O \mid Zn.$$

The quantity dE/dT for this cell [1] is -0.000104; the heat of dilution is 4654 calories per gram molecule (Thomsen). The computed emf would be —

emf due to heat of dilution,

$$\frac{4654}{2 \times 23{,}040} = 0.10100$$

emf at 0° equal to

$$T\frac{dE}{dT} = -273 \times 0.000104 = -0.02839$$

$$E = 0.07261$$

The mean observed emf at 0° was 0.0751 volt.

This concentration cell is precisely like a voltaic cell with a negative temperature coefficient. Its energy is derived from the heat of dilution, and it is difficult to see how the Nernst formula for the emf of a concentration cell can have any application whatever to it.

[1] Phys. Rev., Vol. XXIX, 1909, p. 329.

Since the relation between the thermo-electromotive forces of the two amalgams (§ 9) and the temperature is a linear one, the potential difference at the liquid-amalgam junctions may be computed from the expression $T \cdot dE/dT$. Thus, the potential difference between the zinc sulphate solution and the dilute amalgam (0.6 per cent) at 27° is

$$0.001046 \times 300 = 0.3138 \text{ volt.}$$

For the concentrated amalgam (1.2 per cent) it is

$$0.001017 \times 300 = 0.3051 \text{ volt.}$$

Then the emf of the concentration cell composed of the two amalgams and the zinc sulphate as electrolyte, owing to the thermo-electromotive forces at 27°, is

$$0.3138 - 0.3051 = 0.0087 \text{ volt.}$$

But there is a loss on account of the negative heat of dilution equal to about 0.001 volt. Hence

$$E = 0.0087 - 0.0010 = 0.0077 \text{ volt.}$$

The measured value was 0.0078 volt.

36. A Composite Concentration Cell. — A concentration cell, in which the difference in concentration is entirely in the two electrolytes bathing the electrodes, may be combined with one in which the concentration difference is in the amalgam electrodes in such a manner that the

complete cell may have zero temperature coefficient, and thus come under case one of the general equation.

For example, the cell

$$\text{Zn amal.} \mid ZnSO_4 \cdot 50\, H_2O \mid ZnSO_4 \cdot 190\, H_2O \mid \text{Zn amal.}$$

has an emf represented approximately by the equation

$$E_2 = 0.001527 + 0.00003084\ T.$$

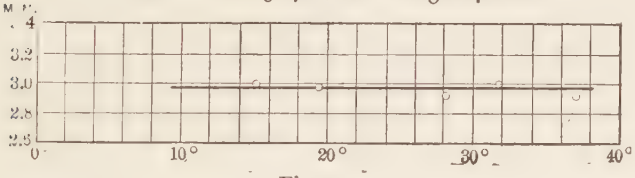


Fig. 24

The positive is the electrode in the more concentrated solution. If this cell be combined with the one whose equation was found to be

$$E_1 = -0.001455 + 0.00003084\ T$$

with the dilute solution in contact with the dilute zinc amalgam, the resulting emf of the combination will be the difference between the two equations representing the two components of the composite cell. Then

$$E_2 = +0.001527 + 0.00003084\ T$$
$$E_1 = -0.001455 + 0.00003084\ T$$
$$E = \quad 0.002982 + 0.0$$

The results of a single trial of such a cell are shown in Fig. 24. The amalgams were the same as those used in getting the data for Fig. 23. The equilibrium of the cell was rather uncertain and was easily disturbed by a jar.

37. A Pair of Calomel Cells with Constant EMF. — The change of emf of the calomel cell with temperature is about 0.1 millivolt per degree and positive. The thermo-electromotive force at the mercury-mercurous chloride surface is thus higher than at the surface of the zinc.

Since the thermo-electromotive force between zinc sulphate and zinc amalgam increases as the concentration of the amalgam decreases, it is apparent that a calomel cell with a negative temperature coefficient is possible. Moreover, if the dilution of the amalgam produces a sufficient range in the thermo-electromotive force at its surface, it should be possible to make a calomel cell with a negative change of emf equal to 0.1 millivolt per degree. Such a cell in series with one set up with 10 per cent zinc amalgam would give a combined emf independent of temperature, at least over a range of 25 or 30 degrees.

A trial was made with a three-legged cell. One outer leg contained a 10 per cent zinc amalgam, the other an amalgam with about 0.8 per

cent zinc; in the middle leg was placed mercury covered with mercurous chloride. The electrolyte was a solution of $ZnCl_2$, specific gravity 1.4. The cell was placed in a water bath and the potential difference between the two amalgams and the mercury as the positive electrode was measured at several temperatures. Let E_1 denote the emf of the cell with the 10 per cent amalgam and E_2 the other. A series of measurements is given in the following table:

Temp.	E_1	E_2	$E_1 + E_2$	$E_1 - E_2$
33.3°	0.99693	0.98456	1.98149	0.01237
30.0°	.99665	.98497	1.98162	.01168
26.3°	.99622	.98528	1.98150	.01094
22.3°	.99579	.98571	1.98150	.01008
18.9°	.99545	.98604	1.98149	.00941
14.2°	.99497	.98655	1.98152	.00842
9.4°	.99449	.98709	1.98158	.00740

These measurements were made within a period of two hours and the values correspond, therefore, to somewhat rapid changes of temperature. Nevertheless, $E_1 + E_2$ remains nearly constant. The value of dE_1/dT is fairly represented by 0.000103 and dE_2/dT by $-$ 0.000103. If $E_1 - E_2$ be denoted by E, then $dE/dT = 0.000206$.

The relation of these ratios to one another and to $E_1 + E_2$ is shown graphically in Fig. 25.

38. Heat of Dilution of Zinc Amalgams. — When an amalgam is diluted by the addition of mercury a thermal change occurs. Similarly

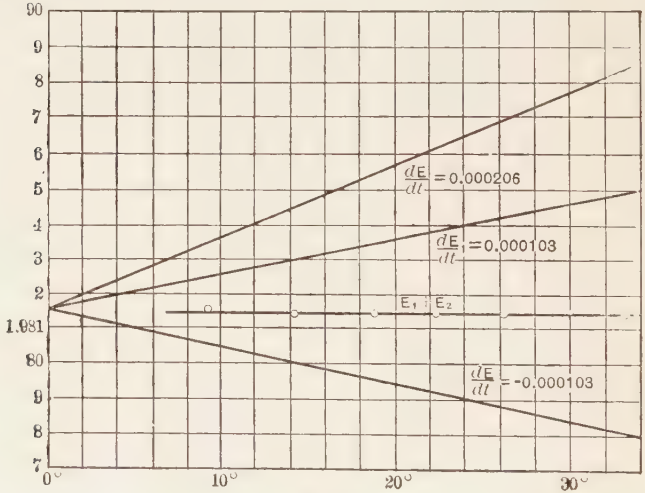


Fig. 25

when a zinc ion is transferred from a more concentrated amalgam to a dilute one, heat is either absorbed or generated. The dilution of a zinc amalgam absorbs heat, that is, the heat of dilution is negative. It follows that when the electrodes of a concentration cell are zinc amalgams of different concentration, the heat of dilution is one

factor determining the emf. Therefore, by measuring the emf and the rate of change of emf with temperature, the Helmholtz equation suffices to measure the heat of dilution for the two amalgams.

The heat of dilution H in joules per gram-molecule appears in the equation

$$E = \frac{H}{nF} + T\frac{dE}{dT}.$$

The cell used for the emf and dE/dT measurements is shown in Fig. 26.[1]

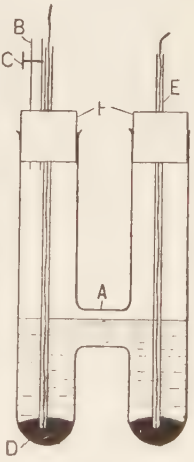


Fig. 26

The cross-connecting tube was large and only partly filled with zinc sulphate solution. Both limbs were closed with rubber stoppers and a stopcock in one served to pump out air and to introduce hydrogen after the amalgams and the solution had been introduced. The cell was first exhausted and then filled with hydrogen, the process being repeated several times, after which it was sealed and immersed in a constant temperature bath. Readings were taken at 0°, 20°, 25°, and 30°, the first only for very dilute amalgams.

[1] Henderson, Phys. Rev., Vol. XXIX, Dec., 1909.

The zinc was deposited electrically in two weighed quantities of mercury, which always had the ratio in mass of 1:2. The concentrations are expressed in percentages of zinc to mercury. For example, 0.2 gm. of zinc in 20 gm. mercury is a concentration of 1 per cent.

For concentrations from 0.5 to about 2 per cent the emf came to a constant value within a few hours after the cell was placed in the 25° bath. An increase in concentration gave a uniform increase in emf and a slight but uniform increase of dE/dT.

TABLE I

Concentration, 0.496 per cent

Date	Notes	Temp.	EMF
March 22, 2:00 P.M.	Cell in 25° bath		
" 6:00 "	"	25.04	0.008383
" 9:00 "	"	25.04	8388
"	Cell successively in baths at 30, 20 and 0 degrees		
" 23, 10:00 A.M.	Cell in 25° bath		
" 1:30 P.M.	"	25.05	8385
" 2:30 "	"	25.03	8380
"	Cell in baths at 30 and 0 degrees		
" 7:00 P.M.	Cell in 25° bath		
" 24, 8:00 A.M.	"	25.05	8387

Table I exhibits the stability of these cells when carried through considerable ranges of temperature.

A summary of the data obtained from cells of fourteen different concentrations is given in Table II. In computing the heats of dilution H, the final constant value of the emf for 25° was substituted for E in the Helmholtz equation.

TABLE II

No.	Conc. of amalgam	EMF	dE/dT	H
	per cent			
1	0.499	0.008360	0.0000280	+ 3
2	0.960	7890	281	− 193
3	1.180	7675	309	− 296
4	1.512	7365	320	− 419
5	1.676	7120	307	− 390
6	1.842	7000	300	− 375
7	1.928	6855	277	− 270
8	2.040	6840	263	− 200
9	2.148	7110	318	− 457
10	2.224	6867	400	− 976
11	2.305	6320	900	− 3960
12	2.412	5730	1710	− 8736
13	2.740	4562	1800	− 9480
14	3.070	3410	1830	− 9920

The data of Table II are plotted in Fig. 27. The curves are regular up to a concentration of a

little more than 2 per cent. At this point occurs a sudden increase in the value of dE/dT; also a downward trend of the emf and a very large and abrupt increase in the negative value of H. These changes are accounted for by the appearance of the solid phase in the dissolved zinc.

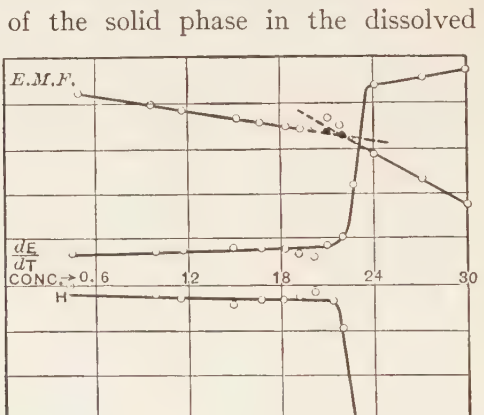


Fig. 27

At 25° the solubility of zinc in mercury is 2.15 per cent. That is, when zinc to the extent of 2.15 per cent of the mercury has been dissolved, zinc is in equilibrium with the zinc amalgam and the solid phase begins to appear. Hence beyond that concentration the value of H includes the heat of liquefaction as well as the heat of dilu-

tion. The entire H-curve is not drawn in the figure because it runs far below the diagram. The measured heat of dilution varies from a negligible value for a concentration of 0.5 per cent to about 10,000 joules per gram ion for 3 per cent.

In this connection it is interesting to note that Lindeck [1] pointed out that zinc and zinc amalgam against zinc sulphate solution show the same potential difference, so long as the mass of zinc in the amalgam exceeds a certain minimum of about 2 per cent. In other words, when the zinc content in the amalgam is above 2.15 per cent, the amalgam acts in a Clark cell precisely like solid zinc.

[1] Wied., Ann., 35, 311 (1888).

CHAPTER VIII

THERMODYNAMICS OF NORMAL CELLS

39. The Clark Cell.[1] — The Helmholtz equation is the fundamental expression for this investigation into the mechanics of the reactions of the Clark cell. The emf and the temperature coefficient of the Clark cell have been so accurately determined that they furnish abundant material for the calculation of H in the Helmholtz equation.

If further H is also to be determined by calorimetric measurements, it is necessary to determine what takes place in the element when F coulombs pass through it. Nernst represented the reaction as follows:

$$Zn + Hg_2SO_4 \rightleftarrows 2\,Hg + ZnSO_4.$$

If this is the correct and complete reaction, then when 2×96500 coulombs have passed through the cell, and one gram ion of zinc has gone into solution, the heat of reaction H should be simply the difference between the heat of

[1] Dr. Ernst Cohen, Zeit. für Phys. Chem., 34, 1900, p. 62.

formation of $ZnSO_4$ and that of Hg_2SO_4. But this leads to an incorrect result because the zinc sulphate takes up seven molecules of water of crystallization and this reaction generates heat. Further, the $ZnSO_4 \cdot 7\,H_2O$ dissolves in water with a thermal change.

The emf of the Clark cell according to Kahle is

$$E_t = E_{15} - 0.00119(t - 15) - 0.000007(t - 15)^2.$$

From this $$\frac{dE}{dT} = -0.00119 - 0.000014(t - 15).$$

Whence at 18° we have

$$\left(\frac{dE}{dT}\right)_{291} = -0.00119 - 0.000042 = -0.001232.$$

and $$E_{18} = 1.4320 - 0.0037 = 1.4283.$$

(1.4320 is the emf at 15°).

If this value of E_{18} is substituted in the Helmholtz equation, the result is

$$1.4283 = \frac{H}{2 \times 96{,}500} - 291 \times 0.001232,$$

or

$$1.7868 = \frac{H}{2 \times 96{,}500}.$$

Whence $H = 344{,}850$ joules.

Now 4.189 joules equal one calorie.

Hence $$H = \frac{344{,}850}{4.189} = 82{,}320 \text{ calories.}$$

According to the Nernst equation for the reaction, the number of calories would be found by subtracting the heat of formation of Hg_2SO_4 from that of $ZnSO_4$. But

Heat of formation of $ZnSO_4$ = 230,090 calories (Thomsen).

Heat of formation of Hg_2SO_4 = 175,000.

The difference is 55,090 calories. This is 27,000 calories less than the number calculated from electrical data.

Since the above does not represent the full reaction, let us seek to find precisely what does occur in the cell.

When $2 \times 96{,}500$ coulombs have passed through the element, one gram-molecule of zinc has gone into solution, united to an equivalent amount of SO_4 from the Hg_2SO_4. The $ZnSO_4$ formed withdraws water from the saturated solution of zinc sulphate to form the hydrated $ZnSO_4 \cdot 7\,H_2O$. This withdrawal of water from the saturated solution takes place in accordance with the equation:

$$ZnSO_4 + \frac{7}{A-7}(ZnSO_4 \cdot AH_2O) = \frac{A}{A-7} ZnSO_4 \cdot 7\,H_2O,$$

where A is the number of molecules of water

associated with one molecule of saturated zinc sulphate at the temperature $t°$ at which the cell is working.

The $ZnSO_4 \cdot 7\,H_2O$ formed crystallizes out in the excess of the salt.

The solubility of $ZnSO_4 \cdot 7\,H_2O$ according to Callendar and Barnes and to Cohen gives $A = 16.81$. Then the above equation becomes

$$ZnSO_4 + 0.713(ZnSO_4 \cdot 16.81\,H_2O) = 1.713\,ZnSO_4 \cdot 7\,H_2O.$$

The heat of formation corresponding to this reaction may be found by supposing the system right and left of the sign of equality diluted by water until both sides have the concentration $ZnSO_4 \cdot 400\,H_2O$. In this manner we get:

Heat of solution of $ZnSO_4$ to $ZnSO_4 \cdot 400\,H_2O$ = 18,430 calories (Thomsen).

The heat of dilution of $ZnSO_4 \cdot 16.81\,H_2O$ to $ZnSO_4 \cdot 400\,H_2O$ is calculated in the following manner:

Heat of dilution of $ZnSO_4 \cdot 20\,H_2O$ to $ZnSO_4 \cdot 50\,H_2O$ = 318 calories (Thomsen).

Hence heat of dilution of $ZnSO_4 \cdot 16.81\,H_2O$ to $ZnSO_4 \cdot 20\,H_2O = \frac{318}{20}(20 - 16.81) = 33.8$ calories.

Then heat of dilution of $ZnSO_4 \cdot 20\,H_2O$ to $ZnSO_4 \cdot 200\,H_2O$ = 390 calories (Thomsen).

Heat of dilution of $ZnSO_4 \cdot 200\,H_2O$ to $ZnSO_4 \cdot 400\,H_2O$ = 10 calories (Thomsen).

$ZnSO_4 - 16.81\,H_2O$ to $ZnSO_4 \cdot 400\,H_2O = 433.6$ calories.

Further the heat of solution of $ZnSO_4 \cdot 7\,H_2O$ to $ZnSO_4 \cdot 400\,H_2O$ = 4260 calories (Thomsen).

Whence for this part of the heat,

$W = 18{,}430 + 0.713 \times 433.8 + 1.713 \times 4260 = 26{,}027$ calories.

Whence $H = 230{,}090 + 26{,}037 - 175{,}000 = 81{,}127$ calories.

This result compares favorably with the 82,320 obtained from electrical data.

40. The Weston Normal Cell.[1] — The scheme of the Weston Normal Cell to which this research applies is as follows:

$Hg - Hg_2SO_4$ – *saturated solution* $CdSO_4 - Cd$ *amalgam* (14.3%).

The cadmium which goes into solution must be withdrawn from the cadmium amalgam. Therefore the heat developed in the cell when $2 \times 96{,}500$ coulombs pass through it is composed of the following portions:

[1] Dr. Ernst Cohen, Zeit. für Phys. Chem., 34, 1900, p. 612.

(*a*) One gram-molecule of Cd must be withdrawn from the amalgam (Heat W_1).

(*b*) The free cadmium combines with SO_4 derived from Hg_2SO_4 to produce $CdSO_4$ (Heat W_2).

(*c*) The $CdSO_4$ formed withdraws water from the saturated cadmium sulphate solution and forms $CdSO_4 \cdot 8/3\ H_2O$, which settles to the bottom in the saturated solution (Heat W_3).

The last reaction takes place in accordance with the equation:

$$CdSO_4 + \frac{8/3}{A - 8/3} CdSO_4 \cdot A\ H_2O$$

$$\frac{A}{A - 8/3} CdSO_4 \cdot 8/3\ H_2O.$$

where A is the number of molecules of water present for each molecule of $CdSO_4$ in the saturated solution at the temperature of the cell.

The total heat developed during the passage of $2 \times 96{,}500$ coulombs is then $W_1 + W_2 + W_3$. W_2 is the difference between the heat of formation of $CdSO_4$ and Hg_2SO_4 and equals

$$219{,}900 - 175{,}000 = 44{,}900 \text{ calories.}$$

The heat W_1 must be experimentally determined electrically. A cell set up as follows served this purpose:

Cd – *solution cadmium sulhpate* – Cd *amalgam* (14.3%).

When the circuit of this cell is closed Cd from the Cd electrode is conveyed to the Cd amalgam. Now by means of the Helmholtz equation and the measurement of the emf of the cell at temperature and by the measurement of the temperature coefficient dE/dT, one can find the heat change when one gram-molecule of Cd dissolves in the amalgam. This value is exactly the same as the one sought but with the opposite sign.

The metallic Cd for the electrode was deposited electrically on a platinum wire from pure cadmium sulphate solution. The amalgam was made by weighing out the component parts. The cell was immersed in a thermostat and the emf measured at 0° and 25°. The emf was measured by the potentiometer method by comparison with a Weston cell and two Clark cells. Two examples of the experimental cell were made and the mean emfs were as follows:

At 25° they were 0.04997 and 0.04989 volt. Mean 0.04993. At 0° they were 0.05579 and 0.05576 volt. Mean 0.05577.

Hence the mean value of dE/dT is

$$\frac{0.04993 - 0.0557}{25} = -0.000233.$$

Then we have the data for 18° $E = 0.0515$; $dE/dT = -0.000233$; $T = 291$. Whence

$W_1 = 2(.0515 + 291 \times 0.000233)\ 23{,}065 = 5503$ calories.

W_1 must then be taken equal to -5503 calories.

Then for W_3 the value of A at 18° is 15.17. Hence the equation becomes

$$CdSO_4 + 0.212(CdSO_4 \cdot 15.17\ H_2O) = 1.212\ CdSO_4 \cdot 8/3\ H_2O.$$

Then assume the quantities on both sides of the sign of equality treated with so much water that the end concentration is $CdSO_4 \cdot 400\ H_2O$ and take the difference in calories.

The following heats of dilution are from the measurements of Holsboer:

$CdSO_4 \cdot 15.6\ H_2O$ to $CdSO_4 \cdot 20.6\ H_2O = 405$ calories
$CdSO_4 \cdot 20.6\ H_2O$ to $CdSO_4 \cdot 30.6\ H_2O = 285$ "
$CdSO_4 \cdot 30.6\ H_2O$ to $CdSO_4 \cdot 50.8\ H_2O = 231$ "
$CdSO_4 \cdot 50\ H_2O$ to $CdSO_4 \cdot 100\ H_2O = 220$ "
$CdSO_4 \cdot 100\ H_2O$ to $CdSO_4 \cdot 200\ H_2O = 171$ "
$CdSO_4 \cdot 200\ H_2O$ to $CdSO_4 \cdot 400\ H_2O = 108$ "

From these we get the required heats of dilution as follows:

$CdSO_4 \cdot 15.17\ H_2O$ to $CdSO_4 \cdot 20.6\ H_2O$

$$= \frac{405}{5}\ 0.43 + 405 = 440 \text{ calories}$$

$CdSO_4 \cdot 20.6\ H_2O$ to $CdSO_4 \cdot 30.6\ H_2O = 285$ calories
$CdSO_4 \cdot 33.6\ H_2O$ to $CdSO_4 \cdot 50\ H_2O = 220$ "
$CdSO_4 \cdot 50\ H_2O$ to $CdSO_4 \cdot 400\ H_2O = 499$ "

Hence heat of dilution $CdSO_4 \cdot 15.17\ H_2O$ to $CdSO_4 \cdot 400\ H_2O = 1446$ calories.

Further, the heat of solution of $CdSO_4$ to $CdSO_4 \cdot 400\ H_2O = 10{,}740$ calories; and the heat of solution of $CdSO_4 \cdot 8/3\ H_2O$ to $CdSO_4 \cdot 400\ H_2O = -2660$ calories.

Therefore $W_3 = 10{,}740 + 0.212 \times 1440 - 1.212 \times 2660 = 7822$ calories.

The total heat change which occurs in the Weston Normal Cell at 18° when $2 \times 96{,}500$ coulombs pass through it is the sum

$$H = W_1 + W_2 + W_3 = -5503 + 219{,}900 - 175{,}000 + 7822 = 47{,}219 \text{ calories.}$$

This value must now be compared with that calculated from the Helmholtz equation with the latest values of E and of dE/dT. The expression for E at $t°$ is

$$E_t = 1.0183 - 0.0000406(t - 20) - 0.00000095(t - 20)^2.$$

So at 18° $E = 1.01838$.

Also $\left(\frac{dE}{dT}\right)_{291} = -0.0000368$

Hence $H = 2(1.01838 + 291 \times 0.0000368)23{,}650$
$= 47{,}471$ calories.

This is to be compared with the 47,219 obtained thermodynamically. The agreement is very good.

The proper reaction for the Weston Normal Cell should be written thus:

$$Cd + \frac{8/3}{A - 8/3}(CdSO_4 \cdot A\ H_2O) + Hg_2SO \rightleftarrows {}_{\text{liquid}}2Hg + \frac{A}{A - 8/3}\underset{\text{solid}}{CdSO_4 \cdot 8/3\ H_2O}.$$

CHAPTER IX

THERMO-EMF WITHOUT TEMPERATURE DIFFERENCE

41. The Rôle Played by Thermo-emf. — Thus far we have applied thermo-emfs to the analysis of the temperature coefficient in a voltaic cell, to the localization of the absorption and generation of heat at the electrodes, to the variation of electromotive force with the concentration of the electrolytes, and to the electromotive force of a simple concentration cell. This view of the temperature coefficient as the difference of the electromotive forces per degree at the two electrodes is sustained by the measurements in a most satisfactory manner, and it has been accepted by those most competent to judge.[1] So also the difference in heating at the electrodes when a current flows through a voltaic cell has been shown mathematically to be an extension of the Gibbs-Helmholtz principle, and the conclusions have been confirmed by quantitative experiments.[2]

[1] Jaeger's Die Normalelemente, p. 38; Cooper's Primary Batteries, p. 53.

[2] Phys. Rev., July, 1900, also Chapter V of this book.

The present inquiry is naturally divided into two parts: first, the existence of thermo-electromotive forces without difference of temperature at the junctions; and, second, the resultant thermo-electromotive forces in a closed circuit.

The Peltier phenomenon is itself sufficient evidence that it is not necessary to heat a junction in order to excite there an electromotive force. In fact this phenomenon is but a single example of a very general law, namely, that when a current flows across any part of a conducting circuit, which is the seat of an electromotive force, energy is either given to the current or is taken from it, according as the electromotive force at the point is directed with the current or against it. Thus, in a direct current motor the current does work against the counter-electromotive force generated by the motor, and the product of the motor is mechanical motion. In a "booster," on the other hand, the generated electromotive force has the same direction as the current, and the current receives energy from the generator. Similar relations obtain in a storage battery. Now unless the devices employed are such that the work done by the current at the seat of an opposing electromotive force takes some other form of energy, the circuit

is invariably heated. In the opposite case, the conductor gives up heat energy and cools. In a Daniell cell, for example, the thermo-electromotive force at either electrode is directed from the electrolyte to the metal. At the zinc, therefore, heat is generated, while at the copper it is absorbed, and the flow of current produces a difference of temperature between the electrolytes surrounding the electrodes. If a current is sent through the cell in the opposite direction, a similar temperature difference is established, but the absorption and generation of heat are then at the opposite electrodes. These temperature changes have nothing to do with the resistance of the cell, and they are proportional to the first power of the current. The direction of the thermo-electromotive force at a copper-iron junction at moderate temperatures is from copper to iron. In accordance then with the general law, when a current is sent across this junction from iron to copper, heat is generated and the junction is heated; if the current passes from copper to iron, heat is absorbed and the junction is cooled. The Peltier effect proves the presence of an electromotive force at the contact of dissimilar substances, and the value of this electromotive force is determined by the usual

thermoelectric experiments. This statement is justified by the measurements made on the Daniell cell before alluded to.

Helmholtz remarks in his celebrated memoir on "The Thermodynamics of Chemical Processes" as follows: "There are besides differences of heating at the two electrodes, which in their manner of appearance are similar to Peltier's phenomena in the case of thermoelectric currents, even though they are perhaps of different origin." The agreement between theory and observation now justifies the statement that they are the same in origin.

A very striking illustration of the general law under which all these facts range themselves, has been brought out by Duddell, in London, within the past few years. He finds an electromotive force between carbon and carbon vapor, and it is directed from the latter to the former. When therefore an arc is formed between carbons, heat is generated at the positive carbon, where the current flows against this thermal electromotive force, and is absorbed at the negative carbon, where it flows in the same direction as the electromotive force there. We have thus an interesting explanation of the higher temperature of the positive carbon.

It is not open to question then that there exists an electromotive force at the junction of two dissimilar substances. The other question remains to be answered. We have been taught that the thermo-electromotive force integrated around a circuit, composed of two or more metals, vanishes when the whole circuit is at one temperature. This law is undoubtedly true for circuits wholly metallic. The denial of it would involve the absurdity of a self-acting thermo-electric engine, continuously converting the heat energy of the surroundings into the energy of an electric current, *without any change in the circuit which would limit the process.* It would be a kind of perpetual motion by which the kinetic energy of diffused heat might be converted into potential energy, or be made more available. The integrated electromotive force around such a circuit therefore vanishes, unless there are differences of temperature.

When the circuit is partly metallic and partly electrolytic, the case is quite different. Imagine a zinc rod bent in the form of a U, and let the two ends be immersed in a solution of zinc sulphate. If now one side of such a cell be slightly warmed, the warmer end of the rod becomes the positive electrode of a thermoelectric cell.

Its electromotive force will be expressed by the equation

$$E = T\left(\frac{dE}{dT}\right)_p - T'\left(\frac{dE}{dT}\right)_n$$

in which T and T' are the temperatures in absolute degrees, of the positive and negative sides respectively. But the flow of current produces changes in the concentrations at the electrodes, with a resulting back electromotive force. If the equalization of concentrations by diffusion is prevented, the above expression finally becomes zero by the decrease of the thermo-electromotive force at the positive electrode, and its increase at the negative.

If two zinc rods joined, let us suppose, by a zinc wire as a resistance, are immersed in solutions of zinc sulphate of different concentrations, the combination is a concentration cell. The current through the cell is from the more dilute to the less dilute solution, and the flow of current acts to equalize the concentrations and reduce the electromotive force. Hence the device as a thermal engine is self-limiting. It can convert some of the equally diffused heat of its surroundings into electric energy, but it can not do so continuously, and can repeat the process only by having the cycle of operations reversed.

42. A Concentration Cell Carried through a Carnot's Cycle. — It may clear our conceptions of such a cell to carry it through a complete Carnot's cycle. Imagine the cell to be contained in a case impervious to heat except through the bottom. Let the porous partition separating the two solutions be a good conductor of heat, but preventing sensible admixture of the liquids. All parts of the cell may then remain at the same temperature. This cell is the working part of a Carnot engine, which includes in addition a conducting stand A at a temperature T, a non-conducting stand B, and a conducting stand C at a lower temperature T'. The usual cycle of four operations may now be carried out.

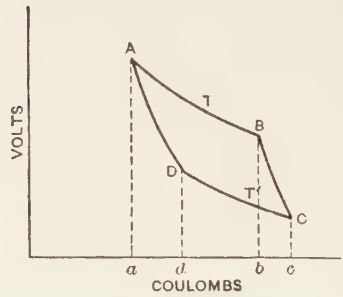


Fig. 28

First. — Place the cell on A and let a small current flow till its electromotive force has fallen from the value denoted by the ordinate Aa in the adjoining figure, to that denoted by Bb, the temperature remaining at the value T by absorption of heat from the stand A. The change in

concentrations causes the decrease of electromotive force, and the cell works along the isotherm AB. Heat is absorbed because the thermo-electromotive force working with the current at the positive electrode is greater than the opposing thermo-electromotive force worked against at the negative. During this operation the work done by the cell is equal to the area $ABba$. The coördinates are electromotive force and quantity of electricity.

Second. — Transfer the cell to the stand B and let the current flow till the electromotive force falls to the value Cc and the temperature to T'. The cell then works along the adiabatic BC. Its temperature falls because the heat absorbed at the positive electrode is still somewhat greater than the heat generated at the negative. The internal resistance of the cell and the current are both supposed to be so small that the heat generated within the cell, proportional to the square of the current, vanishes, and quantities proportional to the first power of the current only are to be considered. In this second operation the electromotive force falls for two reasons, the change in the concentrations and the fall of temperature. The curve BC is therefore steeper than the curve AB. The work

done by the cell during this second stage is represented *BCcb*.

Third. — Transfer the cell to the stand *C* at the temperature *T'*, and pass a reverse or charging current through it at the lower temperature and electromotive force, till the work done on the cell (not on its external circuit) along the lower isotherm *CD* equals the area *CDdc*. This work must be considered as negative. The cell gives out heat to the stand *C*, the reverse current augments the difference of concentrations, and the electromotive force rises.

Fourth. — Transfer the cell to the stand *B* again and continue to pass a charging current till the temperature of the cell rises to *T*. The opposing thermo-electromotive force is now greater than the direct, and heat is generated in the cell. Work done on the cell along this adiabatic *DA* is equal to the area *DAad*.

The cell is completely reversible and has been brought back to initial conditions in all respects. It has the same internal energy, whether chemical or thermal, while the excess of work done by the cell during the entire cycle over the work done on the cell is denoted by the area *ABCD*. This energy is derived from the heat taken in during the first operation with the usual ratio

for the efficiency of a reversible process. The cell works like any other thermodynamic engine, which is carried through a complete cycle of operations, taking in H units of heat at the higher temperature T, and giving out H' units at the lower temperature T'.

A concentration cell carried through such cycles may convert heat into electrical energy indefinitely. So may a steam engine and an electric generator. If the cell does not work in a cycle, its function is then limited to the first operation along the isotherm AB. Gas under pressure in a tank may do the same thing. An essential element is the presence of a stress. In the concentration cell this stress is the difference of the thermo-electromotive forces at the two electrodes. There is no question that there is such a difference, and it is not neutralized by a thermo-emf between the two solutions.

A temperature coefficient is the difference of the thermo-electromotive forces per degree between the metal and the electrolyte at the two electrodes. Whenever a cell has a positive temperature coefficient, it absorbs heat and converts it into electric energy. A concentration cell has an electromotive force proportional to its absolute temperature. It also converts heat

from its surroundings into electric energy. It does it by means of the fact that the thermo-electromotive force at the positive electrode is greater than that at the negative. Its electromotive force is therefore thermoelectric. If any part of its electromotive force is derived from internal energy, such as the heat of dilution, the argument is in no way invalidated. To the extent that it takes in heat from its surroundings and converts it into electric energy, its electromotive force is purely thermoelectric.

It is obvious that any reversible voltaic cell, having a positive temperature coefficient, may be carried through such a cycle as I have described, and the area $ABCD$ will represent the work done by absorbed heat in addition to the work done by the internal energy of the cell. The electric pressure, by means of which this heat energy is transformed, is denoted by the second term of the Helmholtz equation, expressing the electromotive force of a voltaic cell. This term is the integrated value of the thermo-electromotive forces in the circuit. Any voltaic cell with a positive temperature coefficient converts absorbed heat into electric energy; a concentration cell is an extreme type, which absorbs a large part of its electrical output as heat.

INDEX

PAGE

Clark cell 112
Concentration cell carried through a Carnot's cycle 128
composite 102
of two types 20
$\frac{dE}{dT}$ constancy of 96
for the calomel cell 40

EMF due to concentration of amalgams 25
due to a difference in concentration 24
in thermoelectric diagram 9
Experimental cell as a Clark cell 38
Experimental verificaton of heat absorbed and generated .. 52

Heat of dilution of zinc amalgams 106
Helmholtz equation 70

Negative temperature coefficient, case of 101
Nernst and Helmholtz formula for the EMF of concentration cells 67
Nernst equation from thermo-EMF 71
Neutral point 5

Pair of calomel cells with constant EMF 71

PAGE

Research of Mellencamp 79
of Richards and Forbes 74
Reversible heat 1
Reversible voltaic cell 43

Second term of the Helmholtz equation 100

Temperature coefficient of a voltaic cell 28
Thermodynamics, application of 46
of an isothermal process 87
of a voltaic cell 45
Thermoelectric behavior of silver 18
couples 4
diagram 7
power of copper-copper sulphate 33
power of zinc-zinc sulphate 31
Series 10
Thermo-EMF and concentration, relation between 22
between zinc and zinc chloride 12
role played by 122
with amalgams 14

Weston normal cell 116

537.86
C191t

RAYMOND H. FOGLER LIBRARY
DATE DUE

APR 14 '68
FEB 9 1972

UNIV OF MAINE
3 7550 00952585 9

YO-AUP-429